Europäisches Patentamt

European Patent Office

Office européen des brevets

EP 1 029 886 A2

(51) Int. Ct.7: C08J 3/12 **EUROPEAN PATENT APPLICATION** 

23.08.2000 Bulletin 2000/34 (43) Date of publication:

// C08L101:14

(21) Application number: 00102987.5 (22) Date of filing: 14.02.2000

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU Designated Extension States: AL LT LV MK ROSI MC NL PT SE

Akaiwa-gun, Okayama 709-0841 (JP) Himeji-shi, Hyogo 671-1242 (JP)

Ikeuchi, Hiroyuki

Himeji-shi, Hyogo 679-2101 (JP) Suita-shi, Osaka 565-0875 (JP)

Irle, Yoshlo

Ishizaki, Kunihiko

(30) Priority: 15.02.1999 JP 3640799 (71) Applicant:

Osaka-shi, Osaka 541-0043 (JP) Nippon Shokubai Co., Ltd.

Takasago-shi, Hyogo 676-0822 (JP) Hatsuda, Takumi

(2)

Henkel, Feiler, Hånzel 31675 München (DE) M6histrasse 37 Representative: 3

Water-absorbent resin powder and its production process and use B

The absorbent article, according to the present invention, is characterized by comprising an ent resin powder and its production process and use, wherein the water-absorbent resin powder has high liqparticles until the bulk density thereof increases to not according to the present invention, is characterized capacity of not lower than 20 (g/g) for 0.9 weight % addition, the absorbent structure, according to the present invention, is characterized by comprising the above water-absorbent resin powder and a fibrous absorbent layer including the above absorbent struc-The present invention provides a water-absorbpowder, according to the present invention, comprises zation step, and is characterized by further comprising being an arbitrarily pulverized one having a bulk den siclogical saline under a load of 0.7 psi (4.83 kPa) The production process for a water-absorbent resin the step of obtaining water-absorbent crosslinked poly mer particles by way of an aqueous solution polymeri the step of grinding the resultant crosslinked polyme ower than 0.72 (g/ml). The water-absorbent resin pow sity of not lower than 0.74 (g/ml) and a water absorption uid permeability, and further, high water absorbency

Description

**BACKGROUND OF THE INVENTION** 

A. TECHNICAL FIELD

B. BACKGROUND ART

5

The present invention relates to a water-absorbent resin powder and its production process and use.

of sanitary materials, such as disposable diapers, sanitary napkins, and so-called incontinent pads, for the purpose of In recent years, water-absorbent resins (water-absorbing agents) are widely used as constituent materials causing the water-absorbent resins to absorb body fluids

Known examples of the above water-absorbent resins are as tollows: crosslinked polymers of partially neuralized polyacrylic adds; hydrolyzed products of starch-acrylic acid graffed polymers; saponified products of vinyl aceate-acrylic acid ester copolymers, hydrolyzed products of acrylonitrile- or acrylamide copolymers, and their crosslinkod polymers; and crosslinked polymers of cationic monomers.

It is said that the above water-absorbent resins should, for example, have the following properties: upon conlact with aqueous liquids such as body fluids, excellent water absorption quantity and rate, the gel strength, the suction power to suck up water from a base material comtaining aqueous liquids. In addition, a variety of water-absorbent resins or a variety of absorbent structures or articles using the water-absorbent resins are proposed, wherein the water bsorbent resins jointly have a plurality of the above properties and exhibit excellent performance (absorption proper ies) when used for sanitary materials such as disposable diapers and sanitary napkins.

cific diffusing absorbency index under pressure (EP 761,241); and an absorbent structure using a hydrogel that is, for example, characterized by performance under pressure (PUP) and physiological saline flow conductivity (SFC) (USP 5,562,646). In addition, water absorbent resin powders have problems in that they undergo deterioration of the physical ion or thereafter. However, a water-absorbent resin which undergoes such deterioration of the physical properties liftle water absorption rate, and a spedific liquid permeability under a pressure (USP 5,985,944); a water-absorbing agent properties due to surface fracture when (air-)transported or incorporated into absorbent articles in process of producabsorbent resin with a pressure absorbency index (PAI) and a 16-hour extractability level as are regulated (EP naving a specific diffusing absorbancy under prassure (USP 5,760,080); a water-absorbing composition having a spe Known examples of the above water-absorbent resins or absorbent structures or articles using the water absorbent resins are as follows: a water-absorbent resin comprising combinations of a gel volume, a shear modulus and an extractable polymer content as are specified (USP 4.654,039); a water-absorbent resin with a water absorptio using this water-absorbent resin (JP-A-60-185550, JP-A-60-185551, JP-A-60-185804, and USP 4,666,975); disposa ole diapers using a water-absorbent resin having a specific water absorption quantity, a specific water absorption rate and a gel fracture strength as are specified (JP.A.63-099861); disposable diapers containing a water-absorbent resir absorbent composite containing a water-absorbent resin with a water absorbency under a load (AUL) and a particl diameter as are specified (EP 339,461); an absorbert structure containing 60~100 weight % of a specific water-absorb a water-absorbent composite containing at least 30 weight % of water-absorbent resin with a deformation under a load (DUL) and a wicking index (WI) as are specified (EP 532,002); an absorbent article using 30~100 weight % of a water and a gel stability (JP-A-60-185805); water-absorbent articles using a water-absorbent resin with a water absorptio articles containing a water-absorbent resin with a water absorption quantity, a water absorption quantity under a load ent resin with a tree swell rate (FSR) and a water absorbency under a load in 5 minutes as are specified (EP 443,627 615,735); a water-absorbent composite of super-absorbent material with a specific water retention capacity, a specifi quantity, a water absorption rate, and a gel strength as are specified, and disposable diapers and sanitary napkir with a water absorption quantity and a water absorption rate under a load as are specified (JP-A-02-034167), a wate quantity, a suction power, and a water-soluble content as are specified (JP-A-63-021902); water-absorbent sanita \$

with the unimproved properties, and thus such improvements are applied to superabsorbent disposable diapens and so on. However, the liquid permeability between particles of a gel resultant from water absorption of the resin, which is made to ensure the liquid permeability of the gel under a high load (e.g. 0.3 psi (2.07 kPa) corresponding to an Infant's are used, are surely enhanced by adding the above various improvements to water-absorbent resins when compared capacity under a load) of absorbent structures or absorbent articles containing them, for which water-absorbent resins The properties relating to water absorbency (e.g. water absorption capacity under no load, water absorption important for practical daily use, is still at an insufficient level, so it is difficult to say that the whole water-absorbent resin oad), the crosslinking density of the gel needs to be increased at the sacrifice of the water absorbency. and has excellent impact resistance is also known (EP 812,873).

Ş

# SUMMARY OF THE INVENTION

# A, OBJECTS OF THE INVENTION

absorbent resin powder is used. Another object of the present invention is to provide a water-absorbent resin powder wherein the water-absorbent resin powder has high liquid permeability under a load, and further, high water absorbency both under a load and under no load; and further, an absorbent structure and an absorbent article, for which this watterwhich undergoes fittle deterioration of the physical properties and has excellent impact resistance when (air-)trans-An object of the present invention is to provide: a water-absorbent resin powder and its production process, ported or incorporated into absorbent enticles in process of production or thereafter.

# B. DISCLOSURE OF THE INVENTION

The present inventors diligently studied to achieve the above object. As a result, they thought that a cause of insufficient liquid permeability of conventional water absorbent resins was that because particles of such resins have an arbitrarily pulverized shape and therefore have angular or frilly portions in their surfaces, liquid-permeable spaces between particles are non-unitorm in absorbent structures or articles which usually include from tens of thousands up to more than hundreds of thousands of the resin particles. The inventors further thought that the above angular or frilly portions of the particle surfaces are so weak as to deteriorate the impact resistance. 5

of the resultant particles as a means of eliminating the above cause, and actually, the inventors ground the surfaces of the resin particles and then crosslinked the surfaces of the resultant particles, with the result that the inventors found der resultant from the surface grinding was the water-absorbent resin powder which underwent little deterioration of the physical properties and had excellent impact resistance when (air/transported or incorporated into absorbent anticles in process of production or thereafter. Furthermore, the inventors tound that if the above process was used, a novel water absorbent resin powder having high water absorbency and high bulk density was obtainable. In addition, the Then, it occurred to the inventors to grind the surfaces of the resin particles and then crosslink the surfaces that while the water absorbancy was retained at a conventional level, the liquid permeability under a load was greatly inentors found that a water absorbent resin powder, having the arbitrarily pulverized shape and a high bulk density. surprisingly had a rather enhanced liquid permeability between particles under a load in spite of having only a small enhanced when compared with conventional cases. In addition, the inventors found that a water-absorbent resin pow quantity of spaces when packed. Thus, the present invention was completed. ĸ 8

That is to say, an arbitrarily pulverized water-absorbent resin powder, according to the present invention, is characterized by having a bulk density of not lower than 0.74 (g/ml) and a water absorption capacity of not lower than

An absorbent structure, according to the present invention, is characterized by comprising the above arbi-20 (g/g) for 0.9 weight % physiological saline under a load of 0.7 psi (4.83 kPa). S

An absorbent article, according to the present invention, is characterized by comprising an absorbent layer trarity pulverized water ebsorbent resin powder according to the present invention and a fibrous material. including the above absorbent structure according to the present invention.

prises an absorbent layer including the above absorbent structure according to the present invention, wherein the A production process for an arbitrarily pulverized water-absorbent resin powder, according to the present invention, comprises the step of obtaining water absorbent crosslinked polymer particles by way of an aqueous solution polymerization step, and is characterized by further comprising the step of grinding the resultant crossifrised polymer particles until the bulk density thereof increases to not lower than 0.72 (g/ml). Another absorbent article, according to the present invention, is characterized by being a diaper that comabsorbent structure has an arbitrarily pulverized water-absorbent resin powder content of not lower than 30 weight %. 2

These and other objects and the advantages of the present invention will be more fully apparent from the

# BRIEF DESCRIPTION OF THE DRAWINGS

#### [900]

8

Fig. 1 is a flowchart of a typical example of the steps of the present invention production process for a water

Fig. 2 is an imaga which illustrates (A) the shape of the resin powder after pulverization (before grinding) and (B) absorbent resin powder.

S

Fig. 3 is a schematic section of a measurement apparatus as used for measuring the water absorption capacity that after grinding in the present invention. under a load.

## EP 1 029 886 A2

Fig. 4 is a schematic section of a maasurement apparatus as used for measuring the liquid permeation amount

under a load.

Fig. 5 (a) is a vertical schema and Fig. 5 (b) is a horizontal schema of a glass vessel as used for a mechanical dam-

Fig. 6 is a schema of a dispersing machine as used for the mechanical damage test. age test

Fig. 7 is a schema of a bulk density measurement apparatus.

Fig. 9 is an electron micrograph showing the particle structure of a resin powder as obtained in Comparative Exam-Fig. 8 is an electron micrograph showing the particle structure of a resin powder as obtained in Example 1.

# DETAILED DESCRIPTION OF THE INVENTION 9

[0017] Hereinafter, the present invention is explained in detail.

(Production process for water-absorbent resin powder):

5

An example of the steps of the production process for a water-absorbent resin powder according to the present invention is shown in Fig. 1. However, the steps of the production process for a water-absorbent resin powder according to the present invention is not limited thereto.

The production process for a water-absorbent resin powder, according to the present invention, comprises the step of obtaining water-absorbent crosslinked polymer particles by way of an equecus solution polymerization step. and is characterized by further comprising the step of grinding (the surfaces of) the resultant crosslinked polymer par ticles until the bulk density thereof increases to not lower than 0.72 (g/ml). 8

ized shape. This arbitrarily pulverized one is a water-absorbent resin powder that is obtained by pulverizing a gelled or dried product (preferably a dried product) of the crosslinked polymer that is obtained by way of the aqueous solution polymerization step, and this powder comprises pulverized particles of the arbitrary shape (in other words, irregular shape) (e.g. particles of the shape shown in (A) and (B) of Fig. 2). Incidentally, hereinatter, the arbitrarily pulverized Incidentally, the water-absorbent resin powder according to the present invention is of the arbitrarily pulverwater-absorbent resin powder is simply referred to as water-absorbent resin powder.

weight %, still more preferably not higher than 12 weight %, particularly preferably not higher than 10 weight %, are of the crosslinked polymer. In addition, as to the above-mentioned crosslinked polymer, those which have an higher than 15 alone respectively lpha in combinations with each other, but, among them, one of those which have a carboxyl group or of which the main component is acrylic acid and/or a salt (neutralized product) thereof is used as the main component and usually pulverizing it before and/or after this drying. Examples of such crosslinked polymer include at least one yzed products of starch-acrytonitrile grafted polymers; hydrotyzed products of starch-acrytic acid grafted polymers; saponitied products of vinyl acetate acrylic acid ester copolymens; hydrolyzed products of acrylonitrile- or acrylamide copolymens, or their acossimked polymens; modified products of acossimked polywinyl elcohols containing a carboxyl group; and crosslinked isobutylene-maleic anhydride copolymers. These crosslinked polymers may be used either any mixture thereof is preferable, and typically, a polymer which is obtained by polymerizing and crosslinking monomers [0021] The atorementioned crosslinked polymer particles, which are used to produce the water-absorbent resin powder of the present invention, comprise a conventionally known crosslinked polymer that absorbs as large a quantity of water as 50–1,000 times the polymer itself in ion-exchanged water to thareby form an anionic, nonionic, or cationic hydrogel, or the aforementioned crosslinked polymer particles are products by drying (if necessary) the above polymer member selected from the group consisting of: crosslinked polymers of partially neutralized polyacrytic acids; hydrouncrossimked water-soluble content of preferably not higher than 20 weight %, more preferably not i \$ \$ 8 æ

Examples of the above satt of acrylic acid include: alkaline metal salts (e.g. salts of sodium, potassium, and ithium), annnonium salts, and amine salts of acrylic acid. The constituent units of the above-mentioned crosslinkad polacrylic acid of 10-40 mol % and its salt of 90-60 mol % (wherein the total of both is 100 mol %). The neutralization of the crossimked polymer to form the above salt may be carried out either in a monomer state before polymerization or ymer preferably comprise acrylic acid of 0~50 mol % and its salt of 100~50 mol %, and more preferably comprise in a polymer state on the way of polymerization or thereather, or in both states. However, the neutralization in a polymer state needs a considerably long time although such neutralization has the merit of lessening the extractable content. Therefore, in view of the production cost, it is preferable to carry out the neutralization in a monomer state before polym-[0022]

The monomers to give the crosslinked polymer as used in the present invention may further comprise monomers other than the above acrylic acid (and its ealts), if necessary. The monomers other than acrylic acid (and its salts) are not especially limited, but specified examples of them include; anionic unsaturated monomers, such as methacrylic 53

py(meth)acrytamide, N-isopropy(meth)acrytamide, N.N-dimethy!(meth)acrytamide, 2-hydroxyethy! (meth)acrytate, 2-(meth)acryloy/ethanesultonic acid, and 2-(meth)acryloybropanesultonic acid, and their salts; nonionic unsaturated monomers containing a hydrophilic group, such as acrylamide, methacrylamide, N-ethyl(meth)acrylamide, N-n-prohydroxyprapyi (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, polyethylene glycol mono(meth)acrylate inylpyridine, N-vinylpyrrolidone, N-acryloylpiperidine, N-acryloylpyrrolidine, and N-vinylacetamide; cationic unsatuated monomers such as N,N-dimethylaminoethyl (meth)acrytate, N,N-diethylaminoethyl (meth)acrytate, N,N-dimethyl aminopropyl (meth)acrylate, N,N-dimethylaminopropyl(meth)acrylamide, and their quaternary salts. These monomers may be used either alone respectively or in combinations with each other. vinytsutfonic acid, styrenesulfonic acid,

them is preferably not higher than 30 mal %, more preferably not higher than 10 mol %, of the total with acrylic acid and its salts, if the above ratio, then the absorption [0024] In the present invention, when the monomers other than acrylic acid (and its salts) are used, the ratio of properties of the finally resultant water-absorbent resin powder are still more improved, and the water-absorbent resin powder is obtainable at a still lower cost.

polymerization and precipitation polymerization can be carried out. However, considering the performance, the referred to as "aqueous monomar solution") is not especially limited, but is preferably in the range of 10~70 weight %. more preferably 20-40 weight %. In addition, when the above aqueous solution polymerization is carried out, a solvent Examples of the method of the aqueous solution polymerization include: a method in which the aqueous monomer solution is polymerized in a double-erm type kneader while the resultant hydrogel is crushed (in another word, pudverized); and a method in which the equeous monomer solution is supplied into a prescribed vessel or onto easiness of the polymerization control, or the liquid permeability of a swollen gel, it is preferable to carry out aqueous solution polymerization using the above monomer in the form of its aqueous solution. Incidentally, when the monomer is used in the form of its aqueous solution, the concentration of the monomer in its aqueous solution (hereinafter When the above monomer is polymerized to obtain the crosslinked polymer as used in the present invention other than water may be jointly used if necessary, and the kind of the solvent as jointly used is not especially limited. [0025] ž

8

When the above polymerization is initiated, the following radical polymerization initiators, for example, can a moving belt and then polymerized, and the resultant gel is crushed with a tool such as a meat chopper.

ĸ

be used: potassium persultate, ammonium persultate, sodium persultate, t-butyl hydroperoxide, hydrogen peroxide, and 2,2'-azobis(2-amidinopropane) dihydrochloride.

Furthermore, a redox initiator is also available by further using a reductant to promote decomposition of the above polymerization initiator and combining both with each other. Examples of the above reductant include: (bi)suffurous acid salts such as sodium sulfite and sodium hydrogensulfite; L-ascorbic acid (or its salts); reducible metals (or their saits) such as ferrous salts; and amines. However, the reductant is not especially limited to them. [0028] S

by 0.01-0.1 mol %. In the case where the amount of the polymerization initiator is smaller than 0.001 mol %, there are The arrount of the above polymerization initiator as used is usually in the range of 0.001-2 mol %, preferadisadvantages in that a large amount of monomers remain unreacted, so the amount of residual monomers in the resultant polymer increases. On the other hand, in the case where the amount of the polymerization initiator exceeds 2 mol %, there might be disadvantages in that the water-soluble content in the resultant polymer increases. ĸ

In addition, the polymerization reaction may be initiated by irradiating the reaction system with active energy but is preferably in the range of 15-110 °C, more preferably 20-90 °C. In addition, the reaction time is not especially imited either and may filly be set according to factors such as the respective kinds of the monomers and polymerization rays, such as radiations, electron beam, and ultraviolet rays, or by the joint use of this irradiation and the above polymerzation initiators. Incidentially, the reaction temperature in the above polymerization reaction is not especially limited initiators and the reaction temperature.

aossinking agent, but preferable ones are those which are copolymerized or reacted with an internal-crosslinking The crosslinked polymer, as used in the present invention, may be a self-crosslinking type using agent having at least two polymerizable unsaturated groups or at least two reactive groups per molecule. â

Specified examples of the above internal-crosslinking agent include: N,N -methylenebis(meth)acrylamide, potyjettrylene głycol dź(meth)acryłate, (poly)propylene głycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, glycerol tri(meth)acrylate, glycerol acrylate methacrylate, ethylene-oxide-modified trimethylopropane tri(meth)acrylate, pentaerythritol hexa(meth)acytate, triallyl cyanurate, triallyl isocyanurate, triallyl phosphate, triallylamine, poly(meth)allyloxyalkanes, (poly)ethylene glycol diglycidyl ether, glycerol diglycidyl ether, ethylene glycol, polyethylene glycol, propylene glycol, glycerol, pentaerythritol, ethylenediamine, ethylene carbonate, propylene carbonate, polyeth

These internal-crosslinking agents may be used either alone respectively or in combinations with each In addition, these internal-crosslinking agents may be added to the reaction system either all at once or divisionally. When at least one kind or two or more kinds of internal-crosslinking agents are used, it is preferable to essentially use a compound with at least two polymerizable unsaturated groups in the polymerization step, considering the prop-

22

# EP 1 029 886 A2

srties such as absorption properties of the finally resultant water-absorbent resin powder

The amount of the above internal-crosslinking agent as used is preferably in the range of 0.005~2 mol %, nore preferably 0.02–0.5 mal %, still more preferably 0.04~0.2 mal %, of the above monomers. In the respective cases where the amount of the internal-crosslinking agent is smaller than 0.005 mol % and where the amount of the internal crosslinking agent exceeds 2 mol %, sufficient absorption properties might not be obtained.

When the acessinking structure is introduced into internal partions of the polymer using the above internalcrosslinking agent, the internal-crosslinking agent may be added to the reaction system before or on the way of polymerization of the above monomers, or thereafter, or after neutralization.

ous foaming agents such as carbonates (or hydrogencarbonates), carbon dioxide, azo compounds, and inert organic solvents; hydrophilic polymers such as starch, cellulose, their derivatives, polyvinyl alcohol, polyacrylic acid (or its salits), and crosslinked polymers of polyacrylic acid (or its salts); various surfactants; chelating agents; and chain transincidentally, in the above polymerization, the following materials may be added to the reaction system: vari-[9836] 5

When the above-mentioned crosslinked polymer is a product by the aqueous solution polymerization and is a gel, namely, a hydrogelled crosslinked polymer, this crosslinked polymer is dried (it necessary) and usually pulverized fer agents such as hypophosphorous acid (or its salts). 0037

The water content of the crosslinked polymer, usable in the present invention, is not especially limited, but is preferably in the range of 0.1–40 weight % (but not including 40 weight %), more preferably 0.2–20 weight %, still more before and/or after this drying, thus obtaining an arbitrarily purverized crosslinked polymer. 0038

In addition, the particle diameter of the crosslinked polymer, usable in the production process according to the present invention, is usually in the range of 10~1,500 µm, preferably 10~1,000 µm, more preferably 50~800 µm, still mare preferably 75-700 µm (but not including 75 µm), particularly preferably 150-600 µm (but not including 150 preferably 0.5~10 weight %. (003) 8

um), on average.

Next, an explanation is made on the grinding of the atorementioned crosslinked polymer particles, wherein An example of the shape of the water absorbent resin powder which is obtained by the production process the grinding is a feature of the present invention production process for a water-absorbent resin powder. according to the present invention is shown in Fig. 2 (B). <u>§</u> 8

The "grinding" in the present invention is defined as a mechanical unit operation to reduce the specific surparticles. Accordingly, when a comparison is made in the same particle diameter distribution, the conception of the ace area of the polymer particles by fracture or friction which is caused by applying the external force to the polymer [0042] 8

than 0.72 (g/ml). Incidentally, the bulk density, as herein referred to, is defined as the bulk density of particles from which tine powders, as generated (scraped off) by grinding, has been removed. In addition, the removed fine powders may be recovered and then recycled, if necessary (e.g. refer to USP 4,950,692, USP 5,064,582, USP 5,264,485, USP as obtained by drying this gel) by fracture which is caused by applying the external force, such as chopping force (in ation to smooth surfaces of particles having angular or pointed portions, resultant from the pulverization, by eliminating In addition, in other words, the "puliverization" in the present invention is defined as a mechanical operation to reduce the particle diameter of a get resultant from aqueous solution polymerization (or preterably a solid substance other words, dividing force), to the above gel or solid substance, wherein the pulverization is mainly made throughoul or inside the particles. In comparison therewith, the "grinding" in the present invention is defined as a mechanical operconvex portions from such particles, therefore the grinding is mainly made on surfaces of the particles. Then, the prothe step of grinding (surfaces of) the crosslinked polymer particles until the bulk density thereof increases to not lower duction process for a water-absorbent resin powder, according to the present invention, is characterized by comprising prinding" is different from that of the "pulverization" which increases the specific surface area. [0043] 88

Incidentally, the fine powders, as herein referred to, are, for example, particles having particle diameters of not greater than a certain value, for example, 100 µm, preferably 150 µm, more preferably 212 µm. In addition, examples of methods to remove the fine powders include: a method which involves screening with sieves; and a method in which the fine powders are removed by utilizing a gas stream. Incidentally, when the fine powders are removed, the entire removal is difficult due to factors such as classification efficiency, therefore it is enough to remove usually not less than 50 weight %, preferably not less than 70 weight %, more preferably not less than 90 weight %, of the fine powders. in the present invention, the grinding is carried out to the crosslinked polymer particles as obtained by the atorementioned process, and it is preferable to carry out the below-mentioned surface treatment after the grinding. The particle shape of the crosslinked polymer particles resultant from the aforementioned process is an arbitrarily pulverized one, so the crosslinked polymer particles have angular or frilly portions (Fig. 2 (A) and Fig. 9), and are formed into a comparatively roundish shape by the above grinding operation (Fig. 2 (B) and Fig. 8). 5,478,879, EP 812,873, EP 885,917, EP 844,270). <u>8</u> 5 8

Because the polymer particles become more rounded into a uniform shape by the grinding according to the present invention, the bulk density of the ground polymer is higher than that of the unground polymer, and is preferably not lower than 0,72 g/ml, and more preferably in the range of 0,72~0.95 g/ml, still more preferably 0,73~0.90 g/ml, yet ß

still more preterably 0.74–0.90 g/ml, yet still more preferably 0.75–0.90 g/ml, yet still more preferably 0.76–0.90 g/ml, particularly preferably 0.76–0.90 g/ml, most preferably 0.76–0.90 g/ml, in the case where the bulk density of the ground polymer is lower than 0.72 g/ml, there are disabbartainges in that the figuid permeability of the finally resultant absorbent structure or article is not a sufficiently enhanced one, and tuther in that the resistance of the resultant water-absorbent resin powder to the impact (process damage) is inferior. In addition, in the case where the bulk density of the ground polymer is higher than 0.55 g/ml there is a posseibility that it might be difficult to ensure fujuid-permeable spaces between gais when swelling, incidentially, the value of the bulk density in the present invention is measured in a state where the sold content of the polymer (based on the moisture content) is not lower than 95 weight %.

[0047] incidentally, the bulk density (unit; ghril) is a value per unit capacity of the total weight of a plurality of particles when packed in a vessel having a cartain capacity. Then, because there are clearances (gaps) between particles when packed in the vessel, the value of the bulk density is lower than the "density" or "absolute specific gravity" (unit: g/cm?), which is a value of the mass per unit volume of a particle, almost by the gaps.

(10048) In addition, the value of the bulk density is influenced by how to pack the particles (which of ocerse (loose) packing and close (tapped) packing), and further, more or less, the value of the bulk density varies with the type of a

measurement apparatus (bulk density meter).

[0049] Examples of the apparatus to measure the bulk density include those which are represented by UIS K-3362, 13 K-6721, ASTMD 1985-69, or edana APPARENT DENSITY 450, 1-99. The measured values with these apparatus used to the compared with each other. For example, a measured value with an apparatus which is represented by the above adana APPARENT DENSITY 460, 1-20 glernds to be somewhat higher than a measured value with an apparatus which is used in the present invention (an apparatus which is represented by UIS K-3362). In addition, the measured value thrust a when the apparatus which is used in the present invention (an apparatus which is represented by UIS K-3362). In addition, the measured value thrust apparatus when the water-absorbert resin powder is packed into a measurement vessel. In the present invention, the measurement is carried out without giving a vibration or tapping the measurement when the apparatus by a measurement method which are explained in the below-mentioned DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS, is used as the value of the bulk density in the present inven-

(1050) Because the polymer particles become more rounded into a uniform shape by the grinding according to the present timention, the reduction of the average particle diameter (1050) of the ground powher from that of the unground present timention, the reduction of the pulverbation, and is preferably not more than 40 %, more preferably not more than 50 %, still more preferably not more than 15 %. The grinding to exceed 40 % has the disadvantage, for example, not decelerating the water absorption rate or increasing the amount of the generation of fine powders.

8

[0061] The device which is used to carry out the grinding according to the present invention is not especially limited. but devices which can grind the particle surface by mechanically stirring the particles are preferable, and homogenizers so or pin mills are particularly preferable for enabling the achievement of effective grinding, and more preferably highspaced homogenizers are used. The homogenizer is usually a mixing device to form a suspension or emulsion from a two-phase system of solid-figured or infull-juic, but, in the present invention, the homogenizer is found effective for the grinding of the crosslinked polymer particles.

ر باق دوراه ginding or the constitution of properties where the crosslinked polymer is ground with the homogenizer in the present (1062).

7. Per example, in the dash where the crosslinked polymer is ground with the homogenizer in the present (1062). The springing is carried out at preferably 1,000–20,000 rpm, more preferably 3,000–10,000 rpm, for preferably 4.0.

Invention, the grinding is carried out at preferably 1,000–20,000 rpm, more preferably 3,000–10,000 rpm, for preferably 3,000–10,000 rpm, fo

30 seconds ~ 5 hours, more preferably 1 minute ~ 3 hours, still more preferably 3 minutes ~ 2 hours.

[0053] Because, as is afcrementioned, the crossinited polymer particles become more rounded into a uniform shape by the prinding according to the present invention, it quid-permeable spaces can so uniformly exist throughout the resin in absorbent structures or articles, including a plurality of the polymer particles, that the liquid permeability is between particles. The structure or articles including a plurality of the polymer particles, that the liquid permeability is between particles (under a load) can be enhanced in spile of reduction of gaps between particles.

(0654) In addition, because, as is atorementioned, the bulk density (g/ml) of the water-absorbent resin powder is increased by the grinding according to the present invention, merits in the transportation can also be considered, for example, in that a vessel (bag) into which the resultant water-absorbent resin powder is placed can be compact, or in that a large amount of water-absorbent resin powder can be packed into an identical vessel.

rated by the grinding according to the present inventioned, the angular or frilly portions of the polymer particles is eliminated by the grinding according to the present invention, the damage (what is called process damage) of the resis for example due to collistion between resin particles or between the resin and the device in the production process for the resin is lessened, so that the physical properties of the resin can be prevented from deteriorating due to this damage in addition, not only the process damage, but also the damage of the resin during the transportation after production, or only the process damage, but also the damage of the resin during the transportation after production, so or during the production of absorbent articles, or during the practical use (e.g. to disposable dapers) can be reduced, so the deterioration of the physical properties can be prevented. In addition, when compared with conventional particles (water-absorbent resin powder), the ground particles (water-absorbent resin powder), the ground particles (water-absorbent resin powder), the ground particles (water-absorbent resin powder) have better miscibility with surface-rossilinking agents, therefore can be surface.

### EP 1 029 886 A2

crosslinked more uniformly, therefore give the resultant water-absorbent resin powder better absorption properties or hinher oncess damage resistance. (10056) The present invention production process for a water-absorbent resin powder, preferably, further comprises the step of carrying out a surface-crossifinding treatment by further mixing a surface-crossifinding agent with the crossifinded polymer particles (water-absorbent resin powder) resultant from the grinding treatment in the above way. The surface-orossifinding treatment is able to reduce the hormation of itsheyes of particles when absorbing water or to improve the absorption properties under a load. Furthermore, the surface-crossifinding teatment of the crossifinded polymer (water-absorbent resin powder) resultant from the grinding treatment can enhance the iquid permeability under a load without damaging the absorption properties under a load.

pounds such as 1,3-dioxolan-2-one, 4-methyl-1,3-dioxolan-2-one, 4,5-dimethyl-1,3-dioxolan-2-one, 4,4-dimethyl-1,3dioxolan-2-one, 4-ethyl-1,3-dioxolan-2-one, 4-hydroxymethyl-1,3-dioxolan-2-one, 1,3-dioxan-2-one, 4-methyl-1,3epibromohydrin and a-methylepichlorohydrin, and their polyamine adducts (for example, Kymene made by Hercules: polyglycerol, glycerophosphoric acid, 2-butene-1,4-diol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-cyclohexanedimethanol, 1,2-cyclohexanol, trimethylolpropane, diethanolamine, triethanolamine, polyoxypropylene, oxyetnylene-oxypropylene blook oxpolymer, pentaerythritol and sorbitol; epoxy compounds such as ethylene glycol diglycidyl ether, polyethylene glycol diglyddyl ether, glycerol polyglycidyl ether, diglycerol polyglycibyl ether, pol rgiycerol polygiycidyl ether, propylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether and glyciddi. polyamine compounds, such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexarrine and polyethylenimine, and their inorganic or organic saits (for example, azetidinium salts); polyisocyanate compounds such as 2,4-tolylene diisocyanate and hexamethylene diisocyanate; polyoxazoline compounds such as 1,2-ethylenebisoxazoline, polyisopropenyloxazoline, and copolymers thereof; alkylene carbonate comdioxan-2-one, 4,6-dimethyl-1,3-dioxan-2-one and 1,3-dioxopan-2-one; haloepoxy compounds, such as epichlorohydrin, egistered trademark); silane coupling agents such as r-glycidoxypropyltrimethoxysilane and r-aminopropyltriethoxysiane, and polyvalent metallic compounds such as hydroxides and chlorides of zinc, calcium, magnesium, aluminum, ron and zirconium. Among them, the polyhydric alcohols and the alkylene carbonate compounds are preferable in view of the safety in the case where the surface-crosslinking agent remains unreacted. Particularly preferable surface-Examples of the surface-crosslinking agent, usable in the present invention, include: polyhydric alcohol compounds such as ethylene glycol, diethylene glycol, propylene glycol, triethylene glycol, tetraethylene glycol, polyethyl ene giycol, 1,3-propanediol, dipropylene glycol, 2,2,4-trimethyl-1,3-pentanediol, polypropylene glycol, glycerol 0057 5 5 8 æ

crosslinking agents are those which include polyhydric alcohols.

[10059] These surface-crosslinking agents may be used either alcone respectively or in combinations with each other. A water-absorbert resin with still more accessifieding agents are used jointly with each other, a water-absorbert resin with still more excellent all east less is obtainable by combining a first and a second surface-crosslinking agent which have sotubility parameters (SP values) different from each other. Incidentally, the above-mentioned solubility parameter is a value as commonly used as a factor showing the polarity of compounds.

st value as commonly used as a factor showing the polarity of compounds.

10059] The above-mentioned first surface-crossinking agent is a compound which is reactive upon a carboxyl group of the crosslinked polymer (water-absorbent resin powder) and has a solubility parameter of not less than 12.5 (calcm²) <sup>1/2</sup> (10.0256 (JIm²) <sup>1/2</sup>). Examples of the lirst surface-crosslinking agent include ethylene giycol, propylene glycol, organization and surface-crosslinking agent col, giycerol, ethylene carbonate, and propylene carbonate. The above-mentioned second surface-crosslinking agent is a compound which is reactive upon a carboxyl group of the crosslinked polymer (water-absorbent resin powder) as a solubility parameter less than 12.5 (calcm²) <sup>1/2</sup> (10.0256 (JIm²) <sup>1/2</sup>). Examples of the second surface-crosslinking agent include giycerol polyglycidy ether, (polyglycerol polyglycidyl ether, (polyglycerol polyglycidyl ether, sthylene giycol, triethylene giycol, triethylene giycol, tetraethylene giycol, and 14. harbanefinking agent account surface giycol, triethylene giycol, and

ymer (water-absorbent resin powder) standing in a dry state. In the case where the above first surface-crosslinking agent is jointly used with the above second surface-crosslinking agent, the amount of the first surface-crosslinking agent as used is in the range of preferably 0.01-8 weight parts, more preferably 0.1-5 weight parts, and the amount of absorbent resin powder) resultant from the grinding treatment in the present invention, depends on factors such as ally in the range of 0.005~10 weight parts, preferably 0.05~5 weight parts, per 100 weight parts of the crosslinked polthe second surface-crosslinking agent as used is in the range of preferably 0.001-1 weight parts, more preferably amount of the surface-crosslinking agent as used is smaller than 0.005 weight part, the crosslinking density in the absorption properties might not be improved. In addition, in the case where the amount of the surface-crosslinking The amount of the surface-crosslinking agent, as used if necessary for the crosslinked polymer (watercombinations of the crosslinked polymer (water-absorbent resin powder) and the surface-crosslinking agent, but is usu-0.005-0.5 weight parts. If the surface-crosslinking agent is used in the above range, the absorption properties for body fluids (aqueous liquids) such as urine, sweat and menstrual blood can be still more improved. In the case where the neighborhood of the surface of the crosslinked polymer (water-absorbent resin powder) can hardly be raised, and the agent as used exceeds 10 weight parts, the surface-crosslinking agent is excessive, and this is uneconomical, and furâ 8 53

ther, it might be difficult to control the crosslinking density to a proper value, so the water absorption capacity might not

powder) resultant from the grinding treatment is mixed with the surface-crosslinking agent. The amount of water, as absorbent resin powder), but is usually in the range of 0.5~10 weight parts, preferably 0.5~3 weight parts, per 100 weight parts of the solid content of the crosslinked polymer (water-absorbent resin powder). In the case where the amount of water as used exceeds 10 weight %, the water absorption capacity might be decreased. In the case where the amount is smaller than 0.5 weight %, there is a possibility that the water absorption capacity under a load could not In the present invention, it is preferable to use water when the crosslinked polymer (water-absorbent resin used then, is different according to the kind, particle diameter, or water content of the crosslinked polymer (water

alkoxy(poly)ethylene glycol, and tetrahydrofuran; amides such as N,N-dimethylitormamide; and sulfoxides such as dimetry/sultoxide. The amount of the organic solvent as used is different according to the kind or particle diameter of he crossinked polymer (water-absorbent resin powder), but is usually in the range of 0~10 weight parts, preferably 0~5 weight parts, more preferably 0.1-5 weight parts, per 100 weight parts of the crosslinked polymer (water-absorbent gosslinked polymer (water absorbent resin powder) is mixed with the surface-crosslinking agent. Examples of the usade hydrophilic organic solvent includa: alcohols such as methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, bury alcohol, isobury alcohol, t-bury alcohol, and propylene glycol; ketones such as acetone; ethers such as dioxane, In addition, in the present invention, a hydrophilic organic solvent may be used in the case

dispersed in organic solvents such as cyclohexane and pentane. However, examples of processes therefor include a powder), thereby mixing them. Spraying is preferable for such a process, and the size of liquid drops to be sprayed is In the present invention, the mixing of the crosslinked polymer (water-absorbent resin powder) with the surace-acsslinking agent may be carried out in a state where the acosslinked polymer (water-absorbent resin powder) is if necessary; and then spreying or dropping the resultant mixture to the crosslinked polymer (water-absorbent resin preferably not larger than 300 µm, more preferably not larger than 200 µm. A water-insoluble tinely particulate powder process comprising the steps of: mixing the surface-crosslinking agent with water and/or the hydrophilic organic solvent or a surfactant may be allowed to coexist when water is used for mixing. [0063] 8 ĸ

The mixing apparatus favorable for the above mixing needs to be able to generate a great mixing force to ensure the uniform mixing. Preferable examples of the mixing apparatus, usable in the present invention, include: cyfinder type mixers, double-wall cone type mixers, high-speed agitation type mixers, V-character-shaped mixers, ribbon type mixers, screw type mixers, fluidized furnace rotary disk type mixers, gas current type mixers, double-arm type greaders, internal mixers, pulverizing type kneaders, rotary mixers, and screw type extruders. 8

water-absorbent resin powder) resultant from the granding treatment is preferably mixed with the surface-crosslinking In the present invention production process for a water-absorbent resin powder, the crosslinked polymer

19.44 19.55

When the heat treatment is carried out in the present invention, the treatment period of time is preferably in the range of 1~180 minutes, more preferably 3~120 minutes, still more preferably 5~100 minutes. The treatment termperature is preferably in the range of 80-250 °C, more preferably 100-210 °C, still more preferably 120-200 °C. The agent, and then the neighborhood of the surface of the water-absorbent resin powder is crosslinked, when a heat treatneating temperature lower than 80 °C might not only lengthen the heat treatment time and therefore deteriorate the pronent is carried out if necessary. \$ The heat treatment can be carried out using conventional dryers or heating-furnaces, and examples thereof include: channel type mixing dryers, rotary dryers, disk dryers, fluidized-bed dryers, gas-stream type dryers, and infra-

â

ent water absorbent resin powder. In addition, in the case where the treatment temperature is higher than 250 °C, the resultant water-absorbent-resin powder might be damaged, so it might be difficult to obtain what has excellent water

ductivity, but also hinder the uniform crosslinking from being achieved and therefore disable the production of the excel-

than 25 (g/g), yet still more preferably not lower than 27 (g/g), particularly preferably not lower than 28 (g/g), for 0.9 ventional ones, however, the water-absorbent resin powder according to the present invention is excellent in terms of capacity of preferably not lower than 20 (9/9), more preferably not lower than 23 (9/9), still more preferably not lower water-absorbent resin powder which has not yet undergone the below-mentioned mechanical damage test. Unlike con-The above surface-crosslinking treatment gives a water-absorbent resin powder having a water absorption weight % physiotogical saline under a load of 0.7 psi (4.83 kPa). Incidentally, the above physical property is that of a keeping the above physical property, or deteriorating it little, even after having undergone mechanical damage. ed dryer 3

invention, may further comprise the step of giving various functions to the water-absorbent resin powder by adding If necessary, the above production process for a water-absorbent resin powder, according to the present thereto, for example, the following materials: deodorants; antimicrobial agents; perfumes; inorganic fine powders such as silicon dioxide and itianium oxide; foaming agents; pigments; dyes; hydrophilic short fibers; plasticizers; pressure

3

# EP 1 029 886 A2

polymers such as polyethylene glycol and polyethylanimine; hydrophobic polymers such as paraffins; thermoplastic manure; oxidants; reductants; water; salts; chelating agents; fungicides; hydrophilic resins such as polyethylene and polypropylene, and thermosetting resins such as polyester resins and urea resins.

# (Water-absorbent resin powder):

by having a bulk density of not lower than 0.74 (g/ml) and a water absorption capacity of not lower than 20 (g/g) for 0.9 weight % physiological saline under a load of 0.7 psi (4.83 kPa), and is, for example, obtainable by the aforementioned The arbitrarily pulverized water-absorbent resin powder, according to the present invention, is characterized production process according to the present invention, but is not limited by this production process.

As to conventional arbitrarily pulverized water-absorbent resin powders, no other but has a bulk density of ily pulverized water-absorbent resin powder according to the present invention is a novel resin. If the bulk density is not erization, which has a comparatively small partide diameter or is spherical, is difficult to fix to pulp and is therefore unsuitable for absorbent articles, and further, this water-absorbent resin tends to be in the form of closest padding, so the quantity of liquid-permeable space portions between particles is too small, and the liquid permeability (under a load) has needed to be sacrificed by increasing the crosslinking density of the gel or adding an additive, while the liquid per-meability has been sacrificed to ensure high absorption properties (water absorption capacity), therefore it has been difficult to ensure both the water absorbency and the liquid permeability (under a load). However, the water-absorbent lower than 0.74 (g/ml) has been disclosed so far in the case where it has a water absorption capacity of not lower than 20 (g/g) for 0.9 weight % physiological sailine under a load of 0.7 psi (4.83 kPa). Therefore, the atorementioned arbitrar is therefore low. Accordingly, the alorementioned water-absorbent resin powder according to the present invention is a resin which can provide improved results with regard to both performances of the water absorbency and the liquid per meability (under a load). So far, to ensure the liquid permeability of a gel under a high load, the absorption properties lower than 0.74 (g/ml), liquid-permeable spaces are so uniformly distributed throughout the resin that the liquid perme ability can be enhanced. On the other hand, a water-absorbent resin resultant from reversed-phase suspension polym resin powder according to the present invention enables it.

In addition, if the bulk density is not lower than 0.74 (g/ml), there are also merits in the transportation, for damage which the resin particles undergo in practical use is little when the resin is conveyed in the production steps of the water-absorbent resin powder or when diapers are produced. Incidentally, in the present invention it has been found that the increase of the bulk density to not lower than 0.74 (g/ml) further has the unexpected ment of decreasing the example, in that a vessel (bag) into which the resultant water-absorbent resin powder is placed can be compact. Furthermore, there are merits in that excessive uneverness of the resin particles is so little that the process damage or the water-soluble content of the water-absorbert resin powder. [0072] 8

The bulk density of the arbitrarily pulverized water-absorbent resin powder according to the present invention is preferably not lower than 0.75 (g/mt), more preferably not lower than 0.76 (g/mt), still more preferably not lower than 0.78 (g/ml), particularly preferably not lower than 0.79 (g/ml), in view of better liquid permeability under a load and less process damage. In addition, the upper limit of the bulk density is preferably not higher than 0.95 (g/ml), and more (0074) The liquid permeability under a load of 0.3 psi (2.07 kPa) is a liquid permeability between particles of the water-absorbent resin powder in consideration of an infant's weight as applied to absorbent articles such as diapers. It has been found that such a liquid permeability under a load of 0.3 psi (2.07 kPa) is, however, not achieved by waterpreterably not higher than 0.90 (g/ml). In the case where the upper limit exceeds 0.95 (g/ml), there are disadvantages in that the liquid permeability (under a load) might be rather deteriorated, because the particles are too closely packed. absorbent resin powders which merely have high water absorption capacity under the load of 0.3 psi (2.07 kPa). 0073 \$ 35

of JP-A-61-200102). In general, however, the water absorption capacity under a load decreases in proportion as the 0.3 psi (2.07 kPa), this water-absorbent resin powder does not necessarily have high water absorption capacity under a load of 0.7 psi (4.83 kPa). Even if water-absorbent resin powders have the same water absorption capacity under a oad of 0.3 ps), they exhibit different values under a load of 0.7 psi due to factors such as their production processes or incidentally, water-absorbent resin powders having a water absorption capacity of not lower than 20 (g/g) ing a bulk density in the range from about 0.4 up to about 0.7 (g/ml) have been known so far (for example, water-absorbent resin powders having a bulk density in the range of 0.40-0.46 (g/ml) are disclosed in the working example portion oad increases. Therefore, even if a water-absorbent resin powder has high water absorption capacity under a load of under the load of 0.3 psi (2.07 kPa) and water-absorbent resin powders (as have undergone the pulverization step) hav-20

To improve the liquid permeability under a load of 0.3 psi (2.07 kPa), thus, the present inventors enhanced the water absorption capacity of a water-absorbent resin powder under a load of 0.7 psi (4.83 kPa), and further enhanced the bulk density of the resin powder, thereby achieved the above object. That is to say, in the present invenlion, grinding (surfaces of) the crosslinked polymer by the aforementioned method enhances the bulk density of a water absorbent resin powder to a higher value than conventional ones, and further, enhances the water absorption capacity polymeric structures. 55

of the resin powder under a load of 0.7 psi (4.83 kPa) to a higher value than conventional ones, thereby can achieve the improvement upon the liquid permeability under a load of 0.3 psi (2.07 kPa) and further can reduce the process damage to the water absorbeat resin nowder.

In addition, the water absorption capacity of the arbitrarily pulverized water-absorbent resin powder according to the present invention is preferably not lower than 23 (g/g), more preferably not lower than 22 (g/g), particularly preferably not lower than 28 (g/g), for 0.9 weight % physiological selline under a load of 0.7 psi (4.83 kPa). Incidentally, the above physical property is that of a water-absorbent resin powder which has not yet undergone the below-mentioned mechanical damage lest. Unlike conventional ones, however, the water-absorbent resin powder above physical property.

or deteriorating it little, even after having undergone mechanical damage.

[0078] By the same reason as mentioned in the preceding explanation of the production process, the arbitrarily pulliprocess are preceding explanation is preferably that of which the neighborhood verticed water ebsorbent resin powder according to the present invention is preferably that of which the neighborhood of the surface-crosslinking agent that of the surface-crosslinking agent that includes a polyhydric alcond. Specifications, for example, the type of the surface-crosslinking agent or the method for the surface-crosslinking are the same as aforementioned.

the surface-crosslinking, are the same as aforementioned.

[10079] The average particle diameter of the water-absorbent resin powder which is provided by the present invention is preferably in the carge of 150–600 µm, more preferably 300–600 µm. In addition, the content of fine powders than is preferably in the range of 150–600 µm, more preferably 300–600 µm. In addition, the content of fine powders having a particle diameter of not larger than 150 µm is usually not higher than 10 weight %, preferably not higher than having a particle diameter of not larger than 150 µm is usually not higher than 10 weight %.

5 weight %, of the whole water-absorbent resin powder, according to the present invention, further has an table of perferably in the range of £2 and a L-value of perferably not lower than 85 in fightness (lightness index), and an a value preferably in the range of £2 and a b value preferably in the range of 0.9 but in chromaticity (phromaticness index), as measured with a device such as be value preferably in difference metter. In the case where the L. a. or b value deviates from the above range, brown a spectroscopic cool difference metter. In the case where the L. a. or b value deviates from the above range, brown a spectroscopic cool of the water-absorbent coloring lands to be seen on the surface of the water-absorbent resin powder, particularly, when the water-absorbent coloring tends to be seen on the surface of the water stockers is such as a see is not favorable to consumers. The above lighting the theory of properties or determined by actors such as raw materials (e.g. monomers, initiators), purity thereof, or production conditions (e.g. heating temperature or time). but, usually, the alorementioned conditions according to the

present invention may fifty be used.

[pto81] The autherized water-absorbent resin powder, according to the present invention, or the water-absorbent resin powder absorbent resin powder as obtained by the production process, according to the present invention, undergoes fittle absorbent resin powder as obtained by the production process damage (mechanical damage), and exhibits a water absorpdetence in the physical properties due to the process damage (mechanical damage), and exhibits a water absorption of the physical properties due to the preferably not lower than 25 (9g), more preferably not below-mentioned DESCRIPTION OF THE PREFERRED EMBODIMENTS) in addition, the water-soluble content is in the same range as aforementioned, namely, preferably not higher than 20 weight %, more preferably not higher than 15 weight %, still more preferably not higher than 12 weight %, still more preferably not higher than 12 weight %, still more preferably not higher than 12 weight %.

# (Absorbent structure):

hydrophilic liber; and still further a constitution comprising a sheet of the water-absorbent resin powder as shaped by resin powder and the hydrophilic fiber, a constitution of the absorbent structure comprising a homogeneous mixture of the water-absorbent resin powder and the hydrophilic fiber is, for example, preferable for sufficiently displaying effects of the present invention. In this case, the weight ratio of the water-absorbent resin powder to the hydrophilic liber is in the range of usually 20: 80  $\sim$  90 : 10, preferably 30 : 70  $\sim$ 90: 10, more preferably 40 : 60  $\sim$  80 : 20, still more preferably 50 : 50 ~ 80 : 20. Because the water-absorbant resin powder according to the present invention has a ground surface and excellent liquid permeability, it is preterable for allowing the water-absorbant resin powder to display its features at ably not lower than 40 weight %. Examples of such include: a constitution comprising a homogeneous mixture of the water-absorbant resin powder and the hydrophilic fiber; a constitution comprising a layer of a homogeneous mixture of the water-absorbent resin powder and the hydrophilic fiber and a layer of the hydrophilic fiber as laminated on the preceding layer; a constitution comprising a layer of a homogeneous mixture of the water-absorbent resin powder and the hydrophitic liber, a layer of the hydrophilic liber, and the water absorbent resin powder as interposed between these layers; and further a constitution comparising the water-absorbent resin powder as interposed between layers of the combining a specific amount of water with the water-ebsorbent resin powder. Incidentally, the constitution of the absorb-The absorbent structure, according to the present invention, is characterized by comprising the aforemenioned arbitrarily pulverized water-absorbent resin powder according to the present invention and a fibrous material the maximum that the ratio of the water-absorbent resin powder is preferably not lower than 30 weight %, more prefer such as a hydrophilic fiber. In the case where the absorbent structure, for example, comprises the water-absorben

22

### EP 1 029 886 A2

ent structure is not limited to the above-mentioned examples thereof.

[0083] Examples of the above-mentioned favous material include hydrophilic fibers such as: cellulose fibers, for example, mechanical pulp, chemical pulp, semichemical pulp, digested pulp, as obtained from wood; and artificial cellulose fibers, for example, rayon acetates. Among the above-exemplified fibers, cellulose fibers are preferable. In addition, the hydrophilic fibers may comprise synthetic fibers acuch as polyamides, polyesters, and polydefine. Incidentally,

the ithrous material is not limited to the above-exemptified fibers.

[0004] In addition, in the case where the ratio of the fibrous material such as the hydrophilic fiber in the absorbent structures, namely, the hydrophilic fibers, may be allowed to adhere together structure is relatively small, the absorbent structures, namely, the hydrophilic fibers are allowed to adhere together; the strength and the shape retainability using adhesive binders. If the hydrophilic fibers are allowed to adhere together; the strength and the shape retainability of the absorbent structure before or during the use thereof can be enthanced.

[0085] Examples of the above-mentioned adhesive binders include: heat-sealable ithers such as polyoleful fibers [0085] Examples of the above-mentioned adhesive binders include: buttene-ethy/ene copolymers); and adhesive (e.g., polyethy/ene, polypropy/ene, ethy/ene-poropylene copolymers); and adhesive functioners are be used either alone respectively or in contribinations with each other. The emulsions. These adhesive binders may be used either alone respectively or in contribinations with each other. The weight ratio of the hydrophilic fiber and the adhesive binder is preferably in the range of 50/50 to 99/1, more preferably 80/20 to 95/5, still more preferably 80/20 to 95/5.

Trough us abus, sum inverted using the absorbers structure according to the present invention is produced using the aforementioned (1908s). Because the absorbert structure according to the present invention wherein the resin powder is strong to the process water-absorbern resin powder according to the present invention process for the absorbern structure, so the damage, the physical properties are little deteriorated even in the production process for the absorbern structure, so the effects of the water-absorbern resin powder according to the present invention, such as achievement of both high effects of the water-absorbern resin powder according to the present invention, such as achievement of both high effects of the water-absorbern resin powder according to the present invention, such as achievement of both high effects of the water-absorbern resin powder according to the present invention.

### Absorbent article):

[0087] The absorbent article, according to the present invention, is characterized by comprising an absorbent layer including the aforementioned absorbent structure according to the present invention.

rectuding the atorementationed absorbert structure accounts for the properties and the absorbert layer induding the above-men[10083] In the absorbert atricte of the present invention, preferably an absorbert layer induding the above-mentioned absorbert structure is inferpose between a liquid-permeable surface sheat and a liquid-imparmeable back
sheet, but if its permissible that a diffusion layer, helping a liquid diffuse and, for example, comprising normwowen fabrics,
sheet, but if its permissible that a diffusion layer, helping a liquid diffuse and, for example, comprising normwowen fabrics,
callulose, or crosslinked cellulose, is put on the upper face of the absorbert layer or on the back or upper face of the

cellulose, or crosslinked cellulose, is put on the upper face of the absorbeth layer or our or the december.

so suffice sheld.

[0089] Because the absorbent article of the present invention comprises the absorbent layer including the absorbent structure of the absorbent article has accellent where the scorption proporties as ent structure of the absorbent article include saminary well as excellent liquid permeability as mentioned above. Specified examples of the absorbent article include saminary well as excellent liquid permeability as mentioned above. Specified examples of the absorbent article include saminary materials such as disposable dispers, samilary naptine, and so-called incontinence pads, but is not especially initied.

Because the absorbent article has excellent water absorption properties and accellent liquid permeability, it can prevent unine from leaking and can altiford so-called dry feeling in the case where the absorbent article is, for example, a disposable disper. Particularly when the absorbent article according to the present invention, and that the absorbent article comparises an absorbent layer including the absorbent structure according to the present invention, and that the absorbent article comparises an absorbent layer including the absorbent resin powder content of not tower than 30 weight %, more preferably not lower than 60 weight 9, particularly preferably mot lower than 50 weight 7, particularly preferably mot lower than 60 weight 7 proved.

Go weight %.

Go

tioned symbatic resurs with wover nature. The second of the absorber layers in order of the absorber layers or constitution of the absorber layers in order sepacially limited if it has the above-mentioned absorber structure. In addition, the process for producing the absorbernt layer is not especially limited. Furthermore, the method for interposing the absorbernt layer between the liquid-permeable sheet and the liquid-impermeable sheet, namely, the process for producing the absorbernt article, is not especially limited.

process to prouvaing the abovering toward, so the control of the absorbent structure or article by further adding set [0092] incidentally, it is permissible to afford various functions to the absorbent structure or article by further adding materials, such as deodorants, perfumers, various intrograms powders, foaming agents, water, and saits, to the above-mentioned absorbent structure, fibers, fertilizers, coxidents, reductants, chelating agents, water, and saits, to the above-mentioned absorbent structure, [0093] Because the absorbent article according to the present invention comprises the absorbent structure as pro-

duced using the atcrementioned water-absorbent resin powder according to the present invention, this absorbent anticle can provide the effects, which the water-absorbent resin powder according to the present invention has, such as achievement of both high absorbency and high fiquid permeability.

# (Effects and Advantages of the Invention):

enhances the liquid permeability while retaining the water absorbency at a conventional high level in comparison with convertional processes, and further, strengthens the resistance to the mechanical damage. In addition, the water The production process for a water-ebsorbent resin powder, according to the present invention, greatly absorbent resin powder, as obtained by the production process according to the present invention, is a novel resin powder having high water absorbency and high bulk density.

# DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

2

9

Hereinafter, the present invention is more specifically illustrated by the following examples of some preferred embodiments in comparison with comparative examples not according to the invention. However, the invention is not limited to these examples, incidentally, the performances of the polymer and the water-absorbent resin powder were measured by the below-mentioned methods.

ture absorption, it is preferable that the below-mentioned found values are corrected on the water content (e.g. 5 weight %) and then used, or that the water-absorbent resin powder which has absorbed the moisture is dried (for example, such as distribution, preservation, or combination with absorbent articles, it is preferable that the measured values of ple, in the case where the water content (based on the moisture content) of the water-absorbent resin powder is lower than 5 weight %, the measured values may be used as they are without the correction on the water content, but, in the In addition, in the case where the water-absorbent resin powder has absorbed the moisture due to factors the physical properties of the water absorbent resin powder are corrected on the water content, if necessary. For examcase where the water content (based on the moisture content) is not lower than 5 weight % due to factors such as mois-8

under vacuum in a wind-free drying oven of 60 °C) prior to the measurement.

# (Water absorption capacity under no load):

 60 mm) and then immersed into 0.9 wt % physiological saline. Sixty minutes later, the bag was chawn up and then hand, the same procedure was carried out using no water-absorbent resin powder, and the resultant weight WO (g) was measured. Thus, the water absorption capacity (g/g) under no load was calculated from these weights W1 and W0 in First, 0.2 g of water-absorbent resin powder was uniformly placed into a nonwoven-fabric-made bag (60 mm drained at 250 G for 3 minutes with a centrifuge, and the weight W1 (g) of the bag was then measured. On the other accordance with the following equation: 용 я

14. 74)

water absorption capacity (g(g) under no load = (W1 (g) - W0 (g))/(weight (g) of water-absorbent resin powder).

### (Water absorption capacity under load): \$

Hereinatter, first, the measurement apparatus as used for measuring the water absorption capacity under a

As is shown in Fig. 3, the measurement apparatus comprises: a scale 11; a vessel 12 of a predatermined capacity as mounted on the scale 11; an air-inhaling pipe 13; an introducing tube 14; a glass filter 16; and a measureload is explained on the basis of Fig. 3. [6600]

The vessel 12 has an opening part 12a on the top and an opening part 12b on the side. The air-inhaling pipe 13 is inserted in the opening part 12a of the vessel 12, and the introducing tube 14 is fitted to the opening part 12b of ment part 15 as mounted on the glass filter 16. 0100

In addition, the vessel 12 contains a predetermined amount of physiological saline 22. The lower end part of the air-inhaling pipe 13 is submerged in the physiological saline 22. The air-inhaling pipe 13 is set to keep the internal pressure of the vessel 12 nearly atmospheric. The glass filter 16 is formed in a diameter of 55 mm. The vessel 12 and the glass filter 16 are connected to each other through the introducing tube 14 made of silicone resin. In addition, the the vessel 12. [0<u>10</u>]

The measurement part 15 comprises: filter paper 17; a supporting cylinder 18; a wire gauze 19 as attached to the bottom of the supporting cylinder 18, and a weight 20; and the measurement part 15 is formed by mounting the iller paper 17 and the supporting cylinder 18 (bottomed with the wire gauze 19) in this order on the glass liller 16 and urther mounting the weight 20 inside the supporting cylinder 18, namely, on the wire gauze 19. The wire gauze 19 is position and level of the glass filter 16 are fixed relative to the vessel 12.

8

## EP 1 029 886 A2

is set so as to be as high as the level of the lower end face 13a of the air-inhaling pipe 13. An arrangement is made such that a predetermined amount of water absorbent resin powder having a predetermined particle diameter can uniformly nade of stainless steel and formed in 400 mesh (mesh opening size: 38 μm). In addition, the level of the upper face of he wire gauze 19, namely, the level of the contact face of the wire gauze 19 with a water absorbent resin powder 21, be spread onto the wire gauze 19. The weight 20 is adjusted in weight such that a load of 0,7 psi (4.83 kPa) can uni formly be applied to the water-absorbent resin powder 21 on the wire gauze 19.

12. Next, the filter paper 17 was mounted on the glass filter 16, and turther, in parallel with this mounting operation, 0.9 g of water-absorbent resin powder was uniformly spread into the supporting cylinder 18, namely, onto the wire gauze The water absorption capacity of the water-absorbent resin powder 21 under a load was measured with the First, predetermined preparatory operations were made, in which, for example, a predetermined amount of 0.9 wt % physiological saline 22 was placed into the vessel 12, and the air-inhaling pipe 13 was inserted into the vessel measurement apparatus having the above-mentioned constitution. The measurement method is hereinafter explained ള [0183] 2

. Next, the wire gauze 19 (on which the water-absorbent resin powder 21 and the weight 20 were put) of the supporting cylinder 18 was mounted on the filter paper 17 such that the center line of the wire gauze 19 would conform 19, and the weight 20 was put on this water-absorbent resin powder 21. 5

Then, the weight (g) of the physiological saline 22, as absorbed by the water absorbent resin powder 21 over a period of 60 minutes since the supporting cylinder 18 had been mounted on the filter paper 17, was determined from with that of the glass filter 16. [0106]

(g) of the physiological saline 22 as actually absorbed by the water-absorbent resin powder 21 was divided by the In addition, the same procedure as the above was carried out using none of the water-absorbent resin powder 21, and the blank weight, namely, the weight (g) of the physiological saline 22, as absorbed by materials other than the water-absorbent resin powder 21, such as the filter paper 17, was determined from a value as measured with the scale 11 and regarded as the blank value. Next, a correction was made by subtracting the blank value, and the weight weight of the water-absorbent resin powder 21 (0.9 g), thus calculating the water absorption capacity (g/g) under the a value as measured with the scale 11. 8

# (Liquid permeation amount under load):

was swollen with artiticial urine (1) under a load of 0.3 psi (2.07 kPa) for 60 minutes. Next, measurement was made on Mith an apparatus of Fig. 4 used, a water-absorbent resin powder (0.900 g) as uniformly put in a vessel 40 the amount (g) of 0.69 vt % aqueous sodium chloride solution 33 as passed through the resultant swollen gel 44 mainly between particles thereof) under a load of 0.3 psi (2.07 kPa) for 10 minutes.

and a No. 400 stainless wire gauze 42 (mesh opening size: 38 µm) was set at the bottom of a lower portion of the cell 41. A lower portion of a piston 46 had enough openings 47 for the liquid to pass through, and the bottom of the piston 46 is fitted with a glass filter 45 having so good permeability that the water-absorbent resin powder or a swollen gel thereof could not enter the openings 47. The cell 41 was put on a stand to support the cell, and a face of contact of the As to the apparatus of Fig. 4, a glass tube 32 was inserted in a tank 31, and the lower end of the glass tube 32 was positioned such that the 0.59 wt % aqueous sodium chloride solution 33 could be maintained at the level of 5 cm above the bottom of the swollen gel 44 in a cell 41. The 0.69 wf % aqueous sodium chloride solution 33 in the tank 31 was supplied into the cell 41 through an L 34 having a cock. Under the cell 41, there is a vessel 48 to collect the passed liquid, and this collecting vessel 48 was put on an even balance 49. The inner diameter of the cell 41 was 6 cm, [0109]

The measured value was obtained in a way that the amount (g) of the liquid that had flowed for 10 minutes stand with the cell was set on a stainless wire gauze 43 that did not hinder the permeation of the liquid. since the cock 35 was opened was read from the even balance. [010]

The artificial urine (1), which was used above, comprised 0.25 g of calcium chloride dihydrate, 2.0 g of potassium chloride, 0.50 g of magnesium chloride hexahydrate, 2.0 g of sodium sulfate, 0.85 g of ammonium dihydrogenphosphate, 0.15 g of diammonium hydrogenphosphate, and 994.25 g of pure water <u>6</u> \$

#### (Mechanical damage test): 20

bottle made by Yamamura Glass K.K.) of Fig. 5. Then, this vessel was fixed by being put between damps which were itted to a dispersing machine of Fig. 6 (No. 488 dispersing machine for test, made by Toyo Selid Seisekusho K.K.), and a vibration of 750 cpm in vibration-rotation number was given to the vessel by 100 V/60 Hz for 30 minutes. Thereby, the and simultaneously therewith vibrated back and forth by 8 mm each (total 16 mm), whereby the water-absorbent resin An amount of 30 g of water-absorbent resin powder and 10 g of glass beads (soda-lime glass beads of about 6 mm in bead diameter for fractional distillation packing) were put into a glass vessel (trade name. A-29, mayonnaise vessel, which was fixed to the above dispersing machine, is moved right and left at a bit angle of 12.5° each (total 25'). ß

2

[0113] The above impact is a force that is experientially defined as such representing the impact upon the water-absorbert resin powder in its production steps, but the above impact is widely applicable also to the damage during the transportation after production, or during the production of absorbent structures. powder in the vessel is impacted upon.

(Bulk density):

This was measured according to JIS K3362 with a bulk density meter (made by Kuramochi Scientific Instru-[0114]

ment Seisakusho K.K.) of Fig. 7.

(based on the moisture content) was not lower than 95 weight %, and where the temperature was 25  $\pm$  2  $^{\circ}$ C, and where the brim of the receiver, was scraped off with a glass rod. Then, the weight of the receiver containing the sample was dentally, the bulk density was measured under conditions where the solid content of the water-absorbent resin powder An amount of 120 g of sample (water-absorbent resin particles), which had been well-mixed to eliminate the uneverness according to the particle diameter, was placed into a funnel 62 with its damper 61 dosed. Immediately thereatier, the damper 61 was opened to drop the sample into a receiver 63. A portion of the sample, standing above measured with an accuracy of 0.1 g to calculate a bulk density in accordance with the below-mentioned equation. Ind-

Incidentally, in the case where the solid content (based on the moisture content) of the water-absorbent resin powder is lower than 95 weight %, it is preferable that the measurement is carried out after the water-absorbent resin powder has been dried preferably under vacuum in a wind-free drying oven of 60 °C to increase the solid content the relative humidity was in the range of 30-50 %.

(based on the moisture content) to not lower than 95 weight %.

S=(C-A)/B

- bulk density (g/ml)
- weight (g) of the receiver
- capacity of the receiver (100 ml)
- weight (g) of the receiver when containing the sample ပ

8

# (Specific surface area).

741

from the amount of the krypton-mixed gas as eliminated. Incidentally, the adsorption-elimination step of the microcell resin powder (of which the sample comprised particles as beforehand obtained by classification into the range of 650-212 µm or 850-150 µm with sieves) was placed into a microcell (TYPE: QS-400) of about 13 cm3 in capacity, and ing helium gas and 0.1 % krypton gas, and the sample was allowed to adsorb the mixed gas until equilibrium was established. Thereafter, the temperature of the microcell containing the sample was reverted to room temperature, and the mixed gas was eliminated from the sample to determine the specific surface area of the water-absorbent resin powder containing the sample was carried out 3 times to determine the specific surface area (m²(g) of the water-absorbent was determined by the "B.E.T. (Brunauer-Emmett-Teller) single-point method. "Analyte full automatic specific surface area measurement apparatus 4-Sorb U1" (made by Yuasa Ionics Co., Ltd.) was used as the measurement apparatus. First of all, about 5 g of water-absorbent the microcell containing the sample was heated to 150 °C under a nitrogen gas current to degas and dehydrate the sample sufficiently. Next, the microcell containing the sample was cooled to -200 °C under a mixed-gas current includ-The specific surface area of the water-absorbent resin powder resin powder from the average amount. [0117] ß

(Weight-average particle diameter):

resin powder into the range of 850–212 µm or 850–150 µm with sieves (their mesh opening sizes were, for example, 600 µm, 405 µm, 300 µm, 212 µm, 150 µm, 106 µm respectively), was plotted on logarithmic probability paper, from which the weight-average particle diameter (D50) was read. The particle diameter distribution of particles, as obtained by beforehand classifying the water-absorbent 8

(Water content (solid content)): 23 [0119] An amount of 1,000 g of water-absorbent resin powder was placed into an atuminum cup having an inner diameter of \$2 mm and then dried by heating in a wind-free drying oven of 105 °C for 3 hours. The weight loss (g) on

### EP 1 029 886 A2

drying of the powder was regarded as water to determine the water content (weight %) (and calculate therefrom the solid content (weight %))

(Evaluation of color of water-absorbent resin powder):

under set conditions (reflection measurement/appendix powder-paste sample stand (30 mm/s)/standard round white board No. 2/30/p projector pipe for powder-paste as the standard) using a spectroscopic color difference meter (SZ-230 ness index) and a value and b value both in chromaticity (chromaticness index) of the water-absorbent resin powder was measured in terms of L value in lightness (light-The surface color of the water-absorbent resin powder [0120]

COLOR MEASURING SYSTEM) made by Nippon Denshoku Kogyo Co., Ltd.

(Absorption rate of absorbent structure: core acquisition):

with a mixer. Next, the resultant mixture was shaped into a web of the size of 260 mm imes 150 mm. Thus, an absorbent [0121] First, 11.4 g of water-absorbent resin powder and 6.2 g of wood pulp were mixed together in a dry manner 5

On the other hand, artificial urine (2) having the composition of urea 1.9 weight %, NaCl 0.8 weight %, CaO<sub>2</sub> structure (having a water-absorbent resin powder content of 65 weight %) was prepared. [0122]

tion into the whole absorbent structure since the above artificial urine (2) began to be poured, was measured and regarded as the first-time absorption rate (second). Thereafter, the absorbent structure which had been used for the A load of 18 g/cm² was uniformly applied to the whole absorbent structure as above, and further, a cylinder having a clameter of 30 mm and a height of 120 mm was pressed omto a central portion of this absorbent structure to allow the cylinder to stand vertically. Next, 50 g of artificial urine (2) of 25 °C was poured into the cylinder quiddy (at one stroke). Then, a period of time, in which the artificial urine (2) in the cylinder was entirely absorbed from the central porabove messurement was used to repeat the same measurement two times at intervals of 50 minutes, thus measuring 0.1 weight %, and MgSO $_4$  0.1 weight % (the balance was water) was prepared. [0123] 8 ĸ

The faster these absorption raites are (in other words, the shorter the above period of time by the second is), the second-time absorption rate (second) and the third-time absorption rate (second). the higher the liquid diffusibility of the absorbent structure can be evaluated.

(Evaluation of performance of absorbent article: (Kewpie (trademark) doll test)): 33

Sixty-five weight parts of water-absorbent resin powder and 35 weight parts of wood putp were mixed together in a dry manner with a mixer. The resultant mixture was shaped into a web of the size of 120 mm imes 400 mm matic molding device. Then, this web was pressed under a pressure of 2 kg/cm² for 5 seconds, thus obtaining an Next, a back sheet (inquid-impermeable sheet) of a liquid-impermeable polypropylene with a so-called leg were attached to each other in this order with double coated tapes, and two so-called tape tastaners were then provided by pneumatically molding the mixture on a wire screen of 400 mesh (mesh opening size: 38 µm) with a batch type pneuabsorbent structure having a basis weight of about 0.047 g/cm² (water-absorbent resin powder content: 65 weight %). gather, the above absorbent structure, and a top sheet (irquid-permeable sheet) of a liquid-permeable polypropylene [0125] 33

and this doll was laid on its face. Thereafter, a tube was inserted between the absorbent article and the doll to inject 50 g of 0.9 weight % physiological saline every 20 minutes into a position corresponding to where urine was discharged from a human body. Then, this injection operation was ended when the injected physiological saline began leaking without being absorbed by the absorbent article, and the total amount (g) of the physiological saline, which had been This absorbent article was fitted up to a so-called Kewpie (trademark) doll (body length: 55 cm, weight: 5 kg), to the resultant attached product, thus obtaining an absorbent article (diaper). [0127] ð

The above measurement was repeated four times, and the average of the resultant four measured values was determined and regarded as the absorption quantity (g). The larger absorption quantity was evaluated as the better performance of the absorbent article injected until then, was measured. [0128]

(Extractable content):

S

paper, and then the extractable content (weight % relative to the water absorbent resin powder) of the water absorbent exchanged) water, and the resultant mixture was stirred for 16 hours. The resultant swollen gel was liftered with filter resin powder was dispersed into 1,000 ml of deionized (ionresin powder was determined by colloidal titration of water-soluble polymers in the resultant (litrate, that is, extraclable components which had eluted from the water absorbent resin powder. An amount of 0.5 g of water-absorbent 53

# REFERENTIAL EXAMPLE

omer concentration: 33 weight %). As a result, about 1 minute after, a polymerization reaction started. Then, while the in a reaction vessel as prepared by capping a jacketed stainless double-arm type kneader of 10 liters in capacity having two sigmoidal vanes, 2.4 g of ammonium peraultate and 0.12 g of L-ascorbic acid were acided to a reac-tion solution under stirred conditions, wherein the reaction solution was prepared by dissolving 2.50 g of polyethylene gycol diacrylate into 5,500 g of an aquecus solution of sodium acrylate having a neutralization ratio of 75 mol % (monresultant gel is crushed, the polymerization reaction was carried out in the renge of 30-60 °C, and the resultant hydrogelled crossinked polymer (1) was got out 60 minutes after the initiation of the polymerization reaction.

The resultant hydrogelled crosslinked polymer (1) had a finely divided diameter of about 5 mm. This finely divided hydrogelled crosslinked polymer (1) was spread onto a wire gauze of 50 mesh (mesh opening size: 300 µm) and then dried at 150 °C with hot air for 90 minutes to obtain a water-absorbent resin (A) which was a crosslinked pol-[0131] 2

REFERENTIAL EXAMPLE 2-5

% aqueous sodium persultate solution, 2.92 g of 0.5 weight % aqueous Lescorbic acid solution, 3.24 g of 5 weight % aqueous 2.2" ezrobis(2-amidimopropane) dihydrochloride (trade name: V-50, made by Wako Pure Chemical Industries, stirred conditions, wherein the reaction solution was prepared by dissolving 1.97 g of polyethylene glycol diacrylate into 35 weight %), and the reaction solution was degassed with nitrogen. As a result, about 1 minute after, a polymentation reaction was carried out while the lower face of the reaction vessel was in a reaction vessel as prepared by fitting a stainless vat with a thermometer and a cap, 3.24 g of 5 weight Ltd.) solution, and 3.34 g of 0.35 weight % aqueous hydrogen peroxide solution were added to a reaction solution under 2,000 g of an aqueous solution of sodium acrylate having a neutralization ratio of 65 mol % (monomer concentration: cooled to 10 °C, with the result that the reaction system reached the peak temperature (82 °C) of the heat generation in 10 minutes after the initiation of the polymerization reaction. Then, after healing the lower face of the reaction vessel at 60 °C for 20 minutes, the resultant hydrogelled crosslinked polymer (2) was got out. 8 ĸ

eter = 9.5 mm, made by Hingga Seisakusho Co., Ltd.) such that the gel would have a diameter of not greater than about 5 mm. This crushed hydrogelled crosslinked polymer (2) was spread onto a wire gauze of 50 mesh (mesh opening size. 300 µm) and then dried at 170 °C with hot air tor 40 minutes to obtain a water-absorbent resin (B) which was a The resultant hydrogelled crosslinked polymer (2) was crushed with a meat chopper (two blades, die diam-ક્ષ

REFERENTIAL EXAMPLE 3-

ene glycol diacrylate into 2,000 g of an aqueous solution of sodium acrylate having a neutralization ratio of 70 mol % (monomer concentration: 39 weight %), and the reaction solution was degassed with nitrogen. As a result, about 4 min-% aqueous sodium persulfate solution and 3.20 g of 0.5 weight % aqueous L-ascorbic acid solution were acided to a reaction solution under stirred conditions, wherein the reaction solution was prepared by dissolving 4.33 g of polyethylof the heat generation in 16 minutes after the initiation of the polymerization reaction. Then, after heating the lower face utes after, a polymerization reaction started. Then, the polymenization reaction was carried out while the lower face of the reaction vessel was cooled to 15 °C, with the result that the reaction system reached the peak temperature (39 °C) In a reaction vessel as prepared by fitting a stainless vat with a thermometer and a cap, 5.33 g of 20 weight of the reaction vessel at 80 °C for 20 minutes, the resultant hydrogelled crosslinked polymer (3) was got out. \$ В

The resultant hydrogelled crosslinked polymer (3) was crushed with a meat chopper (two blades, die diameter = 16 mm, made by Hingga Seisakusho Co., Ltd.) such that the gel would have a diameter of not greater than about 5 mm. This crushed hydrogelled crosslinked polymer (3) was spread onto a wire gauze of 50 mesh (mesh opening size: 300 μm) and then dried at 170 °C with hot air for 40 minutes to obtain a water-absorbent resin (C) which was a crosstinked polymer. [0135]

â

EXAMPLE 1-

8

ent resin was placed into a homogenizer (high-speed homogenizer, Model: MX-7, made by Nihonseiivi Kaisha Ltd.) and then ground at 6,000 rpm for about 1 hour. The resultant water-absorbent resin was sieved with JIS standard sieves The water-absorbent resin (A), which was a crosslinked polymer as obtained in Referential Example 1, was (mesh opening sizes = 850 μm and 212 μm) to classify the resin into particle diameters of 850-212 μm. The water absorption capacity under no load, the extractable content, the bulk density, and the average particle diameter of the pulverized with a hammer mill (rooster (grate): diameter of opening = 3 mm), and 150 g of the pulverized water absorb-[0136]

B

# EP 1 029 886 A2

esultant arbitrarily pulverized water-absorbent resin powder (1) were measured, and results thereof are shown in Table . In addition, an electron micrograph showing the particle structure of the resultant arbitrarily pulverized water-absorbent resin powder (1) is Fig. 8.

#### EXAMPLE 2-

Kaisha Ltd.) and then ground et 6,000 rpm for 25 minutes. The resultant water-absorbent resin was sieved with JIS ctandard sieves (mesh opening sizes = 850 µm and 212 µm) to classify the resin into particle diameters of 850-212 um. The water absorption capacity under no load, the extractable content, the bulk density, and the average particle clameter of the resultant arbitrarily pulverized water-absorbent resin powder (2) were measured, and results thereof are pulverized with a roll granulator (Model: GRN 1041, made by Nippon Granulator Co., Ltd.), and 150 g of the pulverized water-absorbent resin was placed into a homogenizer (high-speed homogenizer, Model: MX-7, mada by Nihonselik The water-absorbent resin (A), which was a crosslinked polymer as obtained in Referential Example 1, was shown in Table 1. 5

#### EXAMPLE 3-

disintegrated by hand, and 150 g of the pulverized water-absorbent resin was placed into a homogenizer (high-speed The water-absorbent resin (B), which was a crosslinked polymer as obtained in Referential Example 2, was homogenizer, Model: MX-7, made by Nihonselid Kaisha Ltd.) and then ground at 6,000 rpm for about 1 hour. The result ant water-absorbent resin was sieved with JIS standard sieves (mesh opening sizes = 850 µm and 212 µm) to classify the bulk density, and the average particle clameter of the resultant arbitrarily pulverized water-absorbent resin powder the resin into particle diameters of 850-212 µm. The water absorption capacity under no load, the extractable content (3) were measured, and results thereof are shown in Table 1. [0138] 8

#### EXAMPLE 4-

The water-absorbent resin (B), which was a crosslinked polymer as obtained in Referential Example 2, was disintegrated by hand, and 150 g of the pulverized water-absorbent resin was placed into a homogenizer (high-speed homogenizer, Model: MX-7, made by Nihonseiki Kaisha Ltd.) and then ground at 6,000 rpm for about 15 minutes. The resultant water absorbent resin was sieved with JIS standard sieves (mesh opening sizes = 850 µm and 212 µm) to classify the resin into particle diameters of 850-212 µm. The water absorption capacity under no load, the extractable content, the bulk density, and the average particle diameter of the resultant arbitrarily pulverized water-absorbent resin powder (4) were measured, and results thereof are shown in Table 1. [6E10]

#### EXAMPLE 5-

33

ent resin was placed into a homogenizer (high-speed homogenizer, Model: MX-7, made by Nihonselid Kaisha Ltd.) and then ground at 6,000 rpm for about 1.5 hours. The resultant water absorbent resin was sieved with JIS standard sieves (mash opening sizes = 850 μm and 212 μm) to classify the resin into particle diameters of 850-212 μm. The water absorption capacity under no load, the extractable content, the builk density, and the average particle diameter of the The water-absorbent resin (C), which was a crosslinked polymer as obtained in Referential Example 3, was pulverized with a hammer mill (rooster (grate): diameter of opening = 3 mm), and 180 g of the pulverized water-absorbresultant arbitrarily pulverized water-absorbent resin powder (5) were measured, and results thereol are shown in Table 1. In addition, the specific surface area of the resultant arbitrarily pulverized water-absorbent resin powder (5) was measured, with the result that it was  $0.011 \, \mathrm{m}^2/g$ . [0140] â 5

# COMPARATIVE EXAMPLE 1-

eters of 850-212 µm. The water absorption capacity under no load, the extractable content, the bulk density, and the average particle diameter of the resultant comparative arbitrarily pulverized water-absorbent resin powder (1) were measured, and results thereof are shown in Table 1. In addition, an electron micrograph showing the particle structure The water-absorbent resin (A), which was a crosslinked polymer as obtained in Referential Exemple 1, was pulverized with a hammer mill (rooster (grate); diameter of opening = 3 mm), and the resultant water-absorbent resin was sieved with JIS standard sieves (mesh opening sizes = 650 μm and 212 μm) to dassify the resin into particle diamof the resultant comparative arbitrarily puliverized water-absorbent resin powder (1) is Fig. 9. 8 133

# COMPARATIVE EXAMPLE 2-

puiverized with a hammer mill (rooster (grate); diameter of opening = 3 mm), and the resultant water-absorbent resin average particle diameter of the resultant comparative arbitrarily pulverized water-absorbent resin powder (2) were as obtained in Referential Example 2, was was sieved with JIS standard sieves (mesh opening sizes = 850 µm and 212 µm) to classify the resin into particle diameters of 850-212 µm. The water absorption capacity under no load, the extractable content, the bulk density, and the The water-absorbent resin (B), which was a crosslinked polymer measured, and results thereof are shown in Table 1.

# -COMPARATIVE EXAMPLE 3-

pulverized with a hammer mill (100sfer (grate): diameter of opening = 3 mm), and the resultant water absorbent resin eters of 850-212 µm. The water absorption capacity under no load, the extractable content, the bulk density, and the everage particle diameter of the resultant comparative arbitrarily pulverized water-absorbent resin powder (3) were measured, and results thereof are shown in Table 1. In addition, the specific surface area of the resultant comparative The water-absorbent resin (C), which was a crosslinked polymer as obtained in Referential Example 3, was was sieved with JIS standard sieves (mesh opening sizes = 850 µm and 212 µm) to dassify the resin into particle diamarbitrarily pulverized water-absorbent resin powder (3) was measured, with the result that it was 0.023  $m^2 
ho_0$ [0143]

9

8

(g/ml) (g/ml) (g/ml) (g/ml) (g/ml) (g/ml) (0.83 0.87 0.87 0.66 0.66 0.66 0.64		Ę	-Physical properties before surface crosslinking-	sefore surface crosslini	-Bup	
(A) 45 13 0.83 (A) 45 (B) 48 8.3 0.87 (B) 50 10 0.73 (C) 31 9.1 0.87 (A) 46 15 0.66 (B) 5.3 11 0.66 (C) 31 9.1 0.66 (C) 31 9.1 0.66		Water-absorb- ent resin before pulverization or grinding	Water absorption capacity under no load (g/g)	Extractable content (weight %)	Bulk density (g/mi)	Average particle diameter (µm)
(A) 45 14 0.77 (B) 48 8.3 0.67 (C) 31 9.1 0.87 (A) 46 15 0.66 (B) 53 11 0.66 (C) 31 9.7 0.64	Example 1	Æ	45	13	0.83	440
(B) 48 83 0.67 (B) 50 10 0.73 (C) 31 9.1 0.87 (A) 46 15 0.66 (B) 53 11 0.66	Example 2	3	45	14	. 0.77	460
(G) 31 9.1 0.73 (A) 46 15 0.66 (B) 5.3 11 0.66 (C) 31 9.7 0.64	Example 3	(8)	84	8.3	0.87	430
(C) 31 9.1 0.87 (A) 46 15 0.66 (B) 53 11 0.66 (C) 31 9.7 0.64	Example 4	9	S	5	67.0	480
(A) 46 15 0.66 (B) 53 11 0.66 (C) 31 9.7 0.64	Example 5	0	31	9.1	0.87	440
(B) 53 11 0.66 (C) 31 9.7 0.64	Comparative Example 1	<b>(4)</b>	94	ž.	99:0	220
(C) 31 9.7 0.64	Comparative Example 2	(e)	æ	11	99.0	250
	Comparative Example 3	(0)	31	9.7	0.64	260

14,

Comparative Examples 1~3: not involving the grinding step. Examples 1~5: involving the grinding step.

Table 1 shows the comparison of the physical properties before surface crosslinking. The extractable contents in Example 1 (bulk density = 0.83 (g/ml) and Example 2 (bulk density = 0.77 (g/ml) (both of which involve the step 4

0.66 (g/m) (which involves no grinding). Incidentally, the above water absorption capacities under no load in these examples and comparative example are values as given by the immersion for 1 hour, but the saturated values thereof of grinding the water-absorbent resin (A)) have reduced to lower than that in Comparative Example 1 (bulk density = were equal to each other, namely, 46 (g/g). 8

In addition, similarly, the extractable contents in Example 3 (bulk density = 0.87 (g/mt) and Example 4 (bulk density = 0.73 (g/ml) (both of which involve the step of grinding the water absorbent resin (B)) have reduced to lower than that in Comparative Example 2 (bulk density = 0.66 (g/ml) (which involves no grinding). Incidentally, the above water absorption capacities under no load in these examples and comparative example are values as given by the immersion for 1 hour, but the saturated values thereof were equal to each other, namely, 53 (g/g). [0145] 絽

In addition, the specific surface area in Example 5 (bulk density = 0.87 (g/ml) (which involves the step of grinding the water-absorbent resin (C)) has reduced to about half that in Comparative Example 3 (bulk density = 0.64

### EP 1 029 886 A2

(g/m) (which involves no grinding) (0.022 (m²/g) in Comparative Example 3 reduced to 0.011 (m²/g) in Example 5), and further, the extractable content in Example 5 also has reduced to lower than that in Comparative Example 3.

#### EXAMPLE 6-

arbitrarity pulverized water-absorbent resin powder (1) as obtained in Example 1. The resultant mixture was subjected to a heat treatment at 185 °C for 30 minutes to obtain an arbitrarily pulverized water-absorbent resin powder (6). The water absorption capacity under no load, the water absorption capacity under a load, the liquid permeation emount under a load, the solid content, and the bulk density of the resultant arbitrarity pulverized water-absorbent resin powder A surface-crosslinking agent, comprising 0.03 weight parts of ethylane glycol diglycidyl ether, 1 weight part of propylene glycol, 3 weight parts of water, and 1 weight part of 2-propanol, was mixed with 100 weight parts of the (6) were measured, and resuits thereof are shown in Table 2.

#### EXAMPLE 7-

[0148] A surface-cossinhing agent, comprising 0.03 weight parts of ethylene glycol diglycicly ether, 1 weight part of propylene glycol, 3 weight parts of weight parts of 2-propanol, was mixed with 100 weight parts of the to a heat treatment at 185 °C for 30 minutes to obtain an arbitrarily pulverized water-absorbent resin powder (7). The arbitrariy pulverized water-absorbent resin powder (2) as obtained in Example 2. The resultant mixture was subjected water absorption capacity under no load, the water absorption capacity under a load, the liquid permeation emount under a load, the solid coment, and the bulk density of the resultant arbitrarity pulverized water-absorbent resin powder (7) were measured, and results thereof are shown in Table 2. 22

#### EXAMPLE 8-

ĸ

to a heat treatment at 185 °C (or 30 minutes to obtain an arbitrarily pulverized water-absorbent resin powder (8). The A surface-crosslinking agent, comprising 0.03 weight parts of ethylene glycol diglycidyl ether, 1 weight part of propylane glycol, 3 weight parts of water, and 1 weight part of 2-propanol, was mixed with 100 weight parts of the arbitarily pulverized water-absorbent resin powder (3) as obtained in Example 3. The resultant mixture was subjected water absorption capacity under no load, the water absorption capacity under a load, the liquid permeation amount under a load, the solid coment, and the bulk density of the resulant arbitrarily pulverized water-absorbent resin powder (8) were measured, and results thereof are shown in Table 2. [0149] ક્ષ

#### EXAMPLE 9-

88

[0150] A surface-crosslinking agent, comprising 0.03 weight parts of ettrylene glycol diglycidyl ether, 1 weight part of 2-propanol, was mixed with 100 weight parts of the to a heat treatment at 185 °C for 30 minutes to obtain an arbitrarily pulverized water-ebsorbent resin powder (9). The arbitrarity pulverized water-absorbent resin powder (4) as obtained in Example 4. The resultant mixture was subjected water absorption capacity under no load, the water absorption capacity under a load, the liquid permeation amount under a load, the solid content, and the bulk density of the resultant arbitrarity pulverized water-absorbent resin powder (9) were measured, and results thereof are shown in Table 2. ŝ

#### EXAMPLE 10-

(5) as obtained in Example 5. The resultant mixture was subjected to a heat treatment at 195 °C for 25 minutes to obtain an arbitrarily pulverized water-absorbant resin powder (10). The water absorption capacity under no load, the water absorption capacity under a load, the liquid permeation amount under a load, the solid content, and the bulk density of (0151) A surtace-crosslinking agent, comprising 1 weight part of 1,4-butanediol, 3 weight parts of water, and 1 weight part of 2-propanol, was mixed with 100 weight parts of the arbitrarily pulverized water-absorbent resin powder the resultant arbitrarity pulverized water-absorbent resin powder (10) were measured, and results thereof are shown in ħ 20

# COMPARATIVE EXAMPLE 4-

[0152] A surface-crosslinking agent, comprising 0.03 weight parts of ethylene glycol diglycidyl ether, 1 weight part of propylene glycol, 3 weight parts of weight part of 2-propanol, was mixed with 100 weight parts of the comparative arbitrarily pulverized water-absorbent resin powder (1) as obtained in Comparative Example 1. The result-

ant mixture was subjected to a heat treatment at 185 °C for 30 minutes to obtain a comparative arbitrarily pulverized water-absorbent resin powder (4). The water absorption capacity under no load, the water absorption capacity under a load, the irquid permeation amount under a load, the solid content, and the bulk density of the resultant comparative arbitrarily pulverized water absorbert resin powder (4) were measured, and results thereof are shown in Table 2.

# COMPARATIVE EXAMPLE 5-

of propylene glycol, 3 weight parts of water, and 1 weight part of 2-propanol, was mixed with 100 weight parts of the comparative arbitrarity pulverized water absorbent resin powder (2) as obtained in Comparative Example 2. The resultant mixture was subjected to a heat treatment at 185 °C for 30 minutes to obtain a comparative arbitrarily pulverized water-absorbent resin powder (5). The water absorption capacity under no load, the water absorption capacity under a load, the liquid permeation amount under a load, the solid content, and the bulk density of the resultant comparative A surface-crosslinking agent, comprising 0.03 weight parts of ethylene glycol diglycidyl ether, 1 weight part erbitrarily pulverized water-absorbent resin powder (5) were measured, and results thereof are shown in Table 2.

# -COMPARATIVE EXAMPLE 6-

capacity under no load, the water absorption capacity under a load, the liquid permeation amount under a load, the solid content, and the bulk density of the resultant comparative arbitrarily pulverized water-absorbent resin powder (6) weight part of 2-propanol, was mixed with 100 weight parts of the comparative arbitrarily pulverized water-absorbent resin powder (3) as obtained in Comparative Example 3. The resultant mixture was subjected to a heat treatment at 195 °C for 25 minutes to obtain a comparative arbitrarily pulverized water-absorbent resin powder (6). The water absorption A surface-crossinking agent, comprising 1 weight part of 1,4-butanediol, 3 weight parts of water, and 1 were measured, and results thereof are shown in Table 2. [9154]

8

#### Table 2

ĸ

۱۱. زرد

				ALIAN Z			
_			-Physical prop	-Physical properties after surface crosslinking-	ce crosslinking-		
		Water- absorbent resin before pulverization or crinding	Water absorp- tion capacity under no load (9/9)	Water absorp- tion capacity under load (9/9)	Liquid perme- ation amount under load (g)	Solid content (weight %)	Bulk density (g/ml)
- L	Example 6	€	39	24	375	86	0.83
	Example 7	€	æ	24	362	86	0.77
	Example 8	(a)	47	27	519	86	0.86
	Example 9	<u>e</u>	47	8	353	88	0.75
9	Example 10	0	27	58	1081	86	0.85
	Comparative Example 4	€	42	25	175	86	0.68
2	Comparative Example 5	(8)	46	53	560	86	0.67
	Comparative Example 6	(0)	27	56	1009	88	0.64
8	Examples 6-1 Comparative E	Examples 6-10: involving the grinding step. Comparative Examples 4-6: not involving the	Examples 6-10: involving the grinding step. Comparative Examples 4-6: not involving the grinding step.	rinding step.			

emounts under load in Example 6 (bulk density = 0.83 (g/ml) and Example 7 (bulk density = 0.77 (g/ml) (both of which involve the step of ginding the water-absorbent resin (A)) have increased to more than two times that in Comparative Exemple 4 (bulk density = 0.68 (p/mt) (which involves no grinding). In addition, the liquid permeation amounts under load in Example 8 (bulk density = 0.75 (g/mt) (both of which involve the step Table 2 shows the comparison of the physical properties after surface crosslinking. The liquid permeation of grinding the water-absorbent resin (B)) have increased to about two times that in Comparative Example 5 (bulk den-[0155]

ß

8

# EP 1 029 886 A2

sity = 0.67 (g/ml) (which involves no grinding). Furthermore, the liquid permeation amount under Load in Example 10 (bulk density = 0.85 (g/ml) (which involves the step of grinding the water-absorbent resin (C)) has increased by 72 (g) as compared with that in Comparative Example 6 (bulk density = 0.64 (g/ml) (which involves no grinding).

# -COMPARATIVE EXAMPLE 7-

capacity under a load was measured with two kinds of loads (0.3 psi and 0.7 psi). Results thereof are shown in Table 3. parts of the comparative arbitrarily pulverized water absorbent resin powder (1) as obtained in Comparative Example 1. The resultant mixture was subjected to a heat treatment at 180 °C for 15 minutes to obtain a comparative arbitranity ity under a load, the liquid permeation amount under a load, the solid content, and the bulk density of the resultant comparative arbitrarily pulverized water-absorbent resin powder (7) were measured. Particularly, the water absorption A surface-crosslinking agent, comprising 0.015 weight parts of ethylene glycol diglycidyl ether, 0.5 weight parts of propylene glycol, 1.5 weight parts of water, and 0.45 weight parts of 2-propanol, was mixed with 100 weight pulverized water-absorbent resin powder (7). The waler absorption capacity under no load, the water absorption capac 5

#### Table 3

				_
Liquid per Solid con bunk defauly meation tent (weight (g/ml) arrount %) under load (g)		29'0		
Solid con- tent (weight %)		86		
Liquid per- meation amount under load (g)		9		
Water absorption capacity under load (g/g)	0.7 psi	12		,
Water absorption cap under load (g/g)	0.3 psi	33	-	
Water absorption capacity under no load (g/g)		43		
Water- absorbent resin before pul- verization or grinding		æ		
		Compara	tive Example	7
8		8		

(D157) As to the comparative arbitrarily pulverized water-absorbent resin powder (7) of Comparative Example 7 (bulk density = 0.67 (g/ml), the water absorption capacity was 33 (g/g) under a load of 0.3 psi (2.07 kPa), but reduced to 12 (g/g) under a load of 0.7 psi (4.83 kPa). Therefrom it was found that the liquid permeability under a load greatly deteriorated in Comparative Example 7 when compared with Example 6 (Example 6 = 375 (g), Comparative Example 7=40 (g))

8

# -EXAMPLES 11~15 AND COMPARATIVE EXAMPLES 8~10-

જ

The mechanical damage test was carried out for each of the water-absorbent resin powders as obtained in Examples 6-10 and Comparative Examples 4-6. Results thereof are shown in Table 4. 

#### Table 4

_		-Physical pro	-Physical properties after mechanical damage test-	I damage test-	
\$		Water-absorbent resin before pulveri-	Water absorption capacity under no load (9/9)	Water absorption capacity under load (9/g)	Liquid permeation amount under load (g)
	Example 11	(A)	40 (39)	24 (24)	382 (375)
8	Example 12	€)	39 (39)	24 (24)	358 (362)
	Example 13	(B)	48 (47)	28 (27)	519 (519)
	Example 14	(B)	46 (47)	29 (30)	317 (353)
	Example 15	(0)	27 (27)	26 (26)	1081 (1081)
	Comparative Exam-	(A)	41(42)	19 (25)	158 (175)
	Die 8				

### Table 4 (continued)

	-Physical prop	-Physical properties after mechanical damage test-	al damage test-	
	Water-absorbent resin before pulveri- zation or grinding	Water absorption capacity under no load (g/g)	Water absorption capacity under load (9/9)	Liquid permeation amount under load (g)
Comparative Example 9	. (a)	47 (46)	26 (29)	224 (260)
Comparative Example 10	(0)	27 (27)	25 (26)	865 (1009)
	Table 2	o mochanical daman	tect (con Table 2)	!

The values in the parentheses are those before mechanical damage test (see Table 2). Examples 11~15: involving the grinding step. Comparative Examples 8~10: not involving the grinding step.

the arbitrarily pulverized water absorbent resin powders (6)-(10) according to the present invention, which have a bulk the mechanical damage. In comparison therewith, the comparative arbitrarily pulverized water-absorbent resin powders (4)-(6), which have a bulk density of lower than 0.74 (g/ml), undergo great reduction of the water absorption capacity under a lead or the liquid permeation amount under a load due to the mechanical danage. Thus, the subitrarily pulverized water-absorbent resin powder according to the present invention is excellent in that it undergoes little deterioration of the physical properties during the production process therefor, or during the transportation thereafter, or during the Table 4 shows the results of the mechanical damage test as carried out after the surface crosslinking. From the comparison with Table 2 showing the results as obtained before applying the impact, it would be understood that density of not lower than 0.74 (g/ml), undergo little or no deterioration of the physical properties even if they are given production of absorbent articles ×

8

# -EXAMPLE 16 AND COMPARATIVE EXAMPLE 11-

S

The measurement of the absorption rate (core acquisition) of the absorbent structure and the evaluation of the performance of the absorbent article (Kewpie (trademark) doll test) were carried out for each of the water-absorbent resin powders as obtained in Example 6 and Comparative Example 4. The methods for these measurement and evaluation are as aforementioned. Results thereof are shown in Table 5. [0160]

Table 5

B

-Evaluation	of performan	-Evaluation of performance of absorbent structures and articles-	structures and	1 articles-
	4	Absorbent structure	e e	Absorbent article
	\$₹	Absorption rate (second)	ond)	Absorption quantity (g)
	First time	First time Second time Third time	Third time	
Example 16	4	23	28	300
Comparative Example 11	46	111	169	250

ŝ

\$

powder (4) of Comparative Example 4, the periods of time by the second as needed particularly for the second- and Table 5 shows the results of evaluation of performance of absorbent structures and absorbent articles (diader (6) of Example 6 when compared with that using the comparative arbitrarily pulverized water-absorbent resin ture is greatly enhanced. In addition, as to the absorbent article (diaper) using the arbitrarily pulverized water-absorbent resin powder (6) of Example 6 when compared with that using the compared we arbitrarily pulverized water-absorbent pers). As is evident therefrom, as to the absorbent structure using the arbitrarily pulverized water-absorbent resin powthird-time liquid absorptions are both shortened to less than half, therefore the absorption rate of the absorbent strucresin powder (4) of Comparative Example 4, the total absorption quantity (g) of the absorbent article is also improved. [0161] 8

#### EXAMPLE 17-

23

The color was evaluated for the arbitrarily pulverized water-absorbent resin powders (6)~(10) of Examples [0162]

# EP 1 029 886 A2

5-10. As a result, any water-absorbent resin powder exhibited an L value of not lower than 85 (namely, L value = about 88), an a value in the range of ±2 (namely, a value = about -0.6), and a b value in the range of 0~9 (namely, b value = Various details of the invention may be changed without departing from its spirit not its scope. Furthermore, the bregoing description of the preferred embodiments according to the present invention is provided for the purpose of illustration only, and not for the purpose of illustration as defined by the appended claims and their equiv-[0163]

#### Ctalms

- An arbitrarily pulverized water-absorbent resin powder, which has a bulk density of not lower than 0.74 (g) for 0.9 weight % physiological saline under a load of 0.7 psi a water absorption capacity of not lower than 20 (g/g) for 0.9 weight % physiological saline under a load of 0.7 psi (4.83 kPa). 2
- An arbitrarily pulverized water-absorbent resin powder according to daim 1, wherein the bulk density is not lower than 0.76 (g/ml). ď 9
- An arbitrarily pulverized water-absorbent resin powder according to claim 1, of which the neighborhood of the surface is cross linked. બં 8
- An arbitrarily pulverized water-absorbent resin powder according to claim 3, of which the neighborhood of the surface is crosslinked with a surface-crosslinking agent that includes a polyhydric alcohol. 4
- An absorbent article, which comprises an absorbent layer including the absorbent structure as recited in claim 5. 1 and a fibrous material ĸ

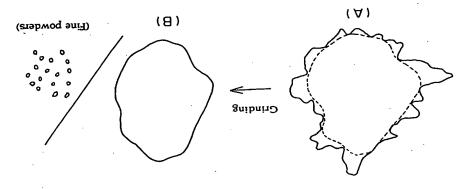
An absorbent structure, which comprises the arbitrarily pulverized water-absorbent resin powder as recited in daim

ιά

- An absorbent article, which is a diaper that comprises an absorbent layer including the absorbent structure as recited in claim 5, wherein the absorbent structure has an arbitrarily pulverized water-absorbent resin powder con-3
- A production process for an arbitrarily pulverized water-absorbent resin powder, which comprises the step of obtaining water-absorbent crosslinked polymer particles by way of an aqueous solution polymerization step, with the process being characterized by further comprising the step of grinding the resultant crosslinked polymer particles until the bulk density thereof increases to not lower than 0.72 (g/ml). tent of not lower than 30 weight %. œί જ્ઞ
- 9. A production process according to claim 8, wherein the step of obtaining the crosslinked polymer particles includes a pulverization step, wherein the pulverization step is carried out simultaneously with the grinding step.
- 10. A production process according to claim 8, wherein the grinding step is carried out under conditions where the specitic surface area of the crosslinked polymer particles can be reduced.
- 11. A production process according to claim 8, which further comprises the step of removing tine powders which are generated in the grinding step. 2
- 12. A production process according to claim 8, which further comprises the step of crosslinking the neighborhood of the surface of the water-absorbent resin powder after the grinding step.
- 13. A production process according to claim 12, wherein the step of crosslinking the neighborhood of the surface of the water-absorbent resin powder involves the use of a surface-crosslinking agent that includes a polyflydric alcohol. 8
- 14. A production process according to claim 12, wherein the step of crosslinking the neighborhood of the surface of the water-absorbent resin powder is carried out until the water absorption capacity of the water-absorbent resin powder for 0.9 weight % physiological saline under a load of 0.7 psi (4.83 kPa) increases to not lower than 20 (9/g). 55

23

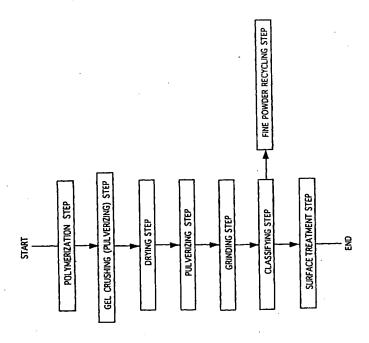
\$



Particles after pulvenzation (before grinding)

Particles after grinding

Fig. 2



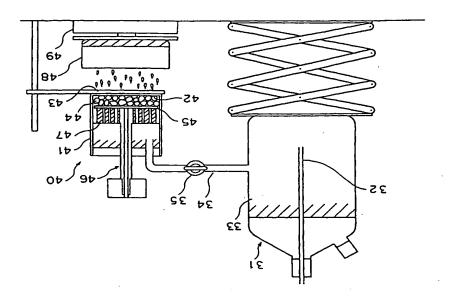


Fig. 4

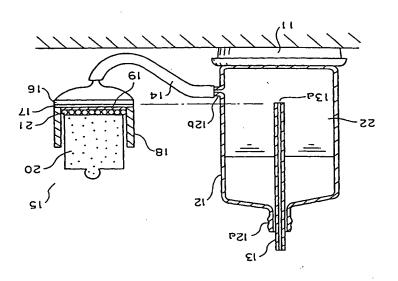


Fig. 3



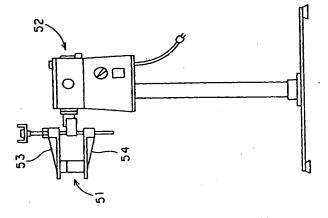
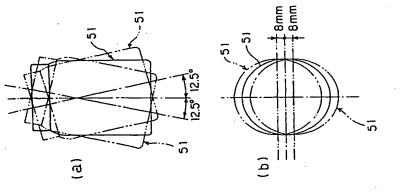
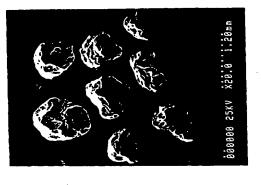


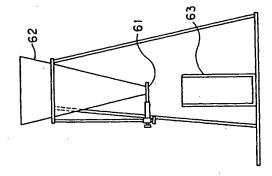
Fig. 6



g



8.8



EP 1 029 886 A2

. .



::

. 6